

# A Review on Emerging Advancements of Nanocellulose and Production Process in Food Packaging Applications

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**ABSTRACT:** In the current strive towards a sustainable future, renewable material resources are increasingly gaining attention and are being investigated for the development of future alternatives to conventional products. This strive is also steadily increasing the demand for new materials with various functionalities and tenable properties. Nanocellulose, a product from renewable materials, has been gaining attention for its utilization in food packaging. This is occasioned by its eco-friendly and biodegradable properties. This review attempts to establish acceptable processes for obtaining nanocellulose and its functionalized form for applications in food packaging. The development and promises of nanocellulose food packaging materials are addressed, together with current challenges and future directions to help transform research developments into commercial products. This review also discussed antibacterial substances utilized in PLA/nanocellulose-based packaging. The latest research on the processing and modification of nanocellulose-based antimicrobial materials against viruses, bacteria, fungi, algae, and protozoa by using variable functional groups is highlighted in this review, which overall focuses on more environmentally friendly food packaging with improved antimicrobial properties. Additionally covered are the issues with industrial manufacture and the potential development of nanocellulose-based antibacterial compounds.

**KEYWORDS:** Nanocellulose; cellulose nanocrystals; cellulose nanofibrils; food packaging; Barrier properties.

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## 1. INTRODUCTION

As the world evolves and becomes more technologically oriented, modern technologies such as nanotechnology contribute to developing society in different fields. The materials we use in our everyday activity have an influence over our whole life culture and economy far more than we are able to accept. The use of localized particles and renewable fibers has received significant attention in the production of hybrid nanocomposites for various applications [1]. This can be recognized by the various transitions when archaeologists talk about the “stone age”, the “bronze age” and the “iron age” [2]. In recent years, there have been a growing number of interests on polymeric materials from renewable sources, especially cellulose. These interests are directly related to an obligation to reduce societal dependence on materials obtained from fossil sources [3].

Brinchi et al., [4] described cellulose as one of the most important natural polymers, a sustainable and inexhaustible material that has been used in the form of wood and plant fibers as energy source, for building materials and for clothing. Nanocellulose (nano-structured cellulose) which is readily available, biodegradable and biocompatible is considered a sustainable material. Nanocellulose exhibits some interesting and unique properties which depend on their size, morphology, charge and other characteristics when broken down into nanometer-scaled particles or fibers [5]. Due to these unique features nanocellulose has gained more attention in the material science community and is considered an attractive candidate for multiple ranges of applications in packaging, biomedical and agricultural. Nanocellulose, especially cellulose nanocrystals (CNC) have many positive characteristics for the

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food packaging industry and their biocompatibility also makes them good candidates for biomedical applications where they can be used in tissue engineering, regenerative medicine and drug delivery [6]. Nanocellulose has been used in many other applications such as in, paper and paper board additives, security papers, paint and coatings etc. fibers [5].

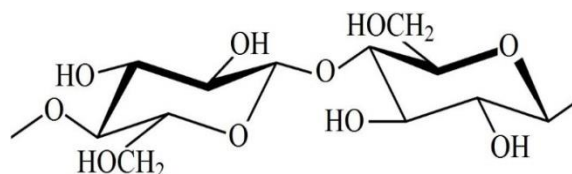
Traditionally, food is packaged for three basic reasons - containment, protection and communication [7]. In order to contain the food product, maintain its quality and inform its consumers, undegradable materials are conventionally used. This however, represents a serious global environmental problem leading to the quest for new bio-based materials that may be edible, biodegradable, and able to extend shelf life and improve quality of food while reducing packaging waste [8]. Though, some researchers have noted performance issues like water sensitivity and limited mechanical properties [9] with high brittleness, which is related to the anarchical growth of amylose crystals with time, it is important to understand and understudy the material properties of nanocellulose.

Typically, nanocellulose from plant source can be classified as either cellulose nanofibrils (CNFs), or cellulose nanocrystals (CNCs) [10]. Cellulose nanofibrils morphology varies from process to process and they often have a wide distribution of diameter and lengths. They are produced by some chemical treatments followed by mechanical refining. Bacteria nanocellulose as the name implies is produced by a species of bacteria generally called *Aceobacterxylinum* [11]. Cellulose nanocrystals are highly crystalline cellulose with discrete, rod-shaped particles which are produced through acid hydrolysis of native cellulose and they have high aspect ratio. However, this paper is focused on nanocellulose advancements for food packaging applications.

## 2. Structure and Morphology of Cellulose

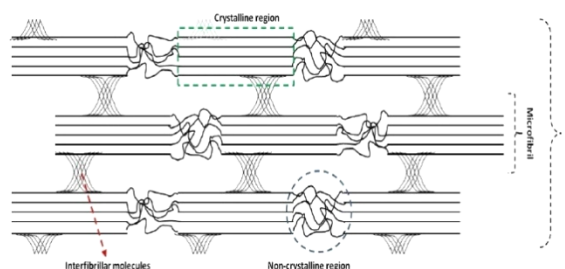
Cellulose is a renewable polymer in the class of polysaccharide and found mostly in plants in materials such as wood, seed and agricultural wastes [12]. Cellulose is also found in the animal kingdom, and to a lesser degree in algae, fungi and invertebrate animals referred to as tunicates [13]. Cellulose has the empirical formula  $(C_6H_{10}O_5)_n$  with large polymer chain and molecular weight. The degree of polymerization and molecular weight of

cellulose-based polymers depend solely on the cellulose origin, approaches and modifications employed during the production of the biopolymer [14]. The number of glucose units or the degree of polymerization is up to 20,000 [15]. Cellulose is classified based on its molecular structure, as a linear condensation polymer formed from linking D-glucose units, which is condensed via the  $\beta$ -1,4-glycosidic bonds, resulting to the formation cellobiose repeat units [16] as seen in Fig. 1.



**Fig. 1: Cellobiose repeat unit from cellulose polymer chains**

Cellobiose contains six membered hydroxyl groups that lead to the formation of inter and intramolecular hydrogen linkages. The intramolecular linkages that exist between the hydroxyl groups of neighbouring glucosides units within the same cellulose molecules are accountable for the stiffness exhibited by the unit chains [17]. The intramolecular hydrogen bonding formed between hydroxyl groups and oxygen of the adjoining ring molecules stabilizes the linkages and results in the linear configuration of the cellulose chain [18]. The morphological hierarchy is defined by elementary fibrils, which pack into larger units called microfibrils, which are in turn assembled into [19]. The degree of cellulose crystallinity is determined by some factors like cellulose origin, in addition to material preparation. Moon et al.[18] reported that within the cellulose fibrils there are regions where the cellulose is orderly arranged and closely packed and regions that are disordered and amorphous as illustrated in Fig. 2.



**Fig. 2: Crystalline and non-crystalline regions in cellulose [20]**

It is these crystalline regions that are extracted to form the cellulose nanocrystals. The inter- and intra-molecular interaction network in the crystalline regions and the molecular orientations can vary, giving rise to cellulose polymorphs or allomorphs, depending on the respective source, method of extraction or treatment [21]. Six inter convertible polymorphs of cellulose have been identified and they are namely I, II, III<sub>I</sub>, III<sub>II</sub>, IV<sub>I</sub> and IV<sub>II</sub>. Review by Habibi et al., [19] gave a more detailed description of cellulose crystallite, among others.

### 2.1. Nomenclature of cellulose nanomaterials

In recent times, advancements of cellulose nanomaterials have gained great attention from researchers and industrial world, together with the principled society due to the exceptional and promising beneficial properties they provide like low coefficient of thermal expansion, high young's modulus, high tensile strength and high surface area-to-volume ratio. The attention is obvious from the number of research papers published together with the large number of patents on the works comprising cellulose nanomaterials, as seen in the literature [22]. According to ISO publications [23-24], cellulose nanomaterials (CNM) are regarded as a kind of nano-objects or materials with one, two or three exterior dimensions in the nanoscale. CNM is a word, frequently used to define nanoscale of a cellulose material, which is believed to be within the nanoscale class, if the fibril particle diameters or width is between 1 to 100 nm. Fig. 3 elucidates the varied categorized structure of cellulose nanomaterials. It is worthy of note that irregularities still exist with regard to the categorization and terminologies functional to CNM.

Lately, the Technical Association of the Pulp and Paper Industry (TAPPI) launched a nanotechnology division which was devoted to cellulose nanomaterials definitions regulation. For the first nanomaterials standard (TAPPI WI 3021: Standard Terms and their Definition for Cellulose Nanomaterials) a blueprint has been drafted and comments are undergoing reviews (Standard Terms, WI [25]. The current literature proposes that a great number of terminologies are presently assigned to cellulose nanomaterials, which inappropriately results in uncertainties and misinterpretations. Apparently, size, aspect ratio, morphology and crystallinity are properties used to differentiate

cellulose particles [26]. Various terminologies have been employed to denote cellulose nanomaterial fundamentals which include nanoscale cellulose, cellulose microfibrils, nanocellulose, cellulose nanofibers, cellulose nanofibrils, nanocellulosic fibrils, nano-sized cellulose fibrils and cellulose nanoparticles. As presented in Fig. 3, nanoscale cellulose may be split into nanostructured materials and nanofibers according to the different isolation approaches employed [27]. The nanostructured materials obtained from cellulose are usually classified into microcrystalline cellulose (or cellulose microcrystals) and cellulose microfibrils [25]. The cellulose nanofibers, on the other hand, are sub-divided into: (a) cellulose nanofibrils (CNF) with different terminologies that have been in use comprising mostly nanofibrillated cellulose (NFC), nanofibrillar cellulose (NFC), cellulosic fibrillar fines (CFF), nanoscale-fibrillated cellulose (NFC), nanofibers (NF), nanofibrils (NF), fibril aggregates (FA) and at times, microfibrillated cellulose (MFC) or microfibrils (MF) [28-32] and (b) cellulose nanocrystals (CNC) with varying terms under use such as nanocrystalline cellulose (NCC), cellulose whiskers (CW), rodlike cellulose crystals (RCC), cellulose nanowhiskers (CN), cellulose crystallites (CC), nanorods and nanowires [33-35]. Bacteria nanocellulose (BNC) and Algae cellulose (AC) a bundle of multi-sized cellulose microfibril that is held strongly by hydrogen bond to form a crystalline structure is known as microcrystalline cellulose [36]. MCC has particle size ranging from 10-50  $\mu\text{m}$  in diameter. It is a commercially available material for food and pharmaceutical industry and also has been utilized as reinforcement filler for polymer composite [18].

MFC contains multiple fibrils with high surface area, high aspect ratio (20-60 nm in diameter and length of several micrometers) with the amorphous and crystalline region segregated [37-38]. Several other terms have been used in place of MFC such names are microfibrillar cellulose, microfibrillized cellulose and cellulose fibrillar fines [39,34].

NFC is a finer cellulose fibril obtained as a result of distinctive techniques incorporating to expedite fibrillation in the mechanical refining of cellulose. NFC has a high aspect ratio (4-20 nm wide and several micrometers in length) with both amorphous and crystalline regions. The fibrillated processes which produce finer

particles are the difference between NFC and MFC. These processes include the high-pressure homogenization, grinding, cryocruising or high intensity ultrasonication [18].

CNCs are highly crystalline particles with high aspect ratio (3-5 nm wide and 50-500 nm in length) and are produced by acid hydrolysis of cellulose [40]. Cellulose nanocrystals have also been called cellulose nanowhiskers by Rosa et al.[41], rodlike cellulose microcrystal [42].

Bacterial nanocellulose formed as a cellulose membrane possessing high purity, does not require secondary treatment to remove

lignins or hemicellulose as in the case of cellulose from lignocellulosic sources. It is produced by bacteria which belong to the genera *Acetobacter*, *Agrobacterium*, *Acaligenes*, *Pseudomonas* and *Sarcina* [43].

Algae cellulose (AC) possesses high crystallinity upon modification via acid hydrolysis, which is similar to CNC obtained from wood sources. Although the rod-like appearance witnessed in CNC is not found in AC. The nanofibrils are about 20 nm wide and are similar in length with those of wood-based cellulose [44,19].

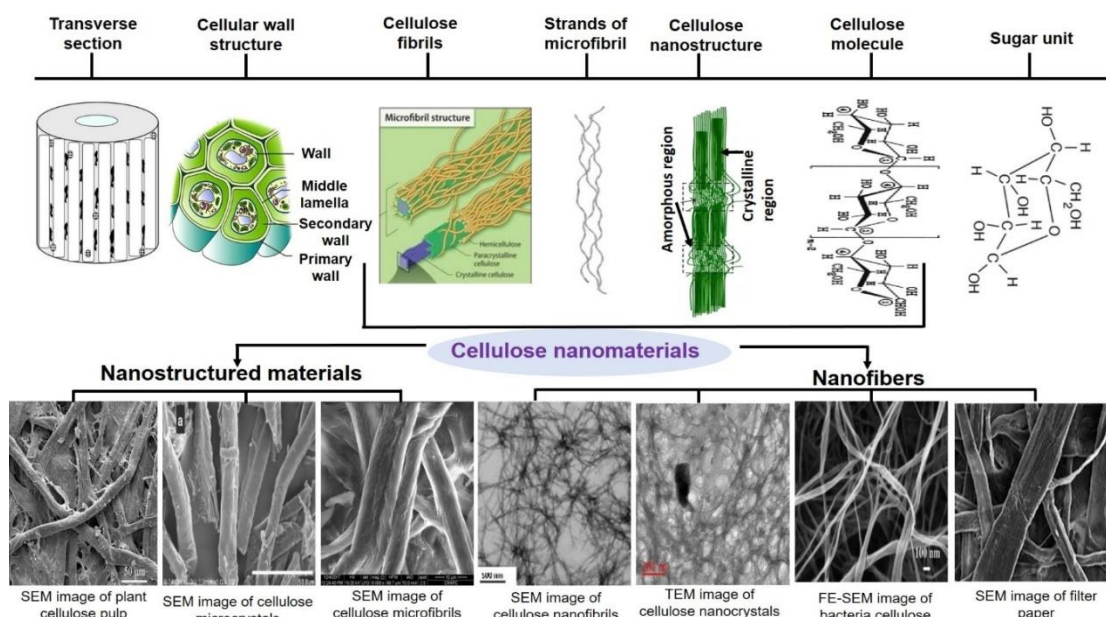


Fig. 3: Different cellulose particle sizes [10, 45-50]

### 3. Preparation of Nanocellulose

Cellulose nanocrystals are formed during the acid hydrolysis of cellulose fibers and they generally have widths of about 2-30 nm and could be several hundreds of nanometers in length. Cellulose structures exist as disordered regions embedded in crystalline or ordered regions or vice versa, during hydrolysis the acid diffuses the glycosidic bonds. After these, more easily accessible glycosidic bonds in the polymer are hydrolyzed and finally hydrolysis occurs at the reducing end group and at the surface of the nanocrystals [51]. Prior to acid hydrolysis, pre-treatment of cellulose materials could take place. For wood and plants, it involves the complete or partial removal of matrix materials. On the other hand, CNFs preparation requires solid mechanical machining. Nevertheless, following the properties of raw materials and degree of

processing, chemical pretreatments need to be conducted before mechanical machining [52]. Actually, appropriate pretreatments of cellulose fibers may elevate the interior surface, change crystallinity and break down hydrogen bonds of cellulose. Several strategies have been employed in cellulose nanofibrils preparation.

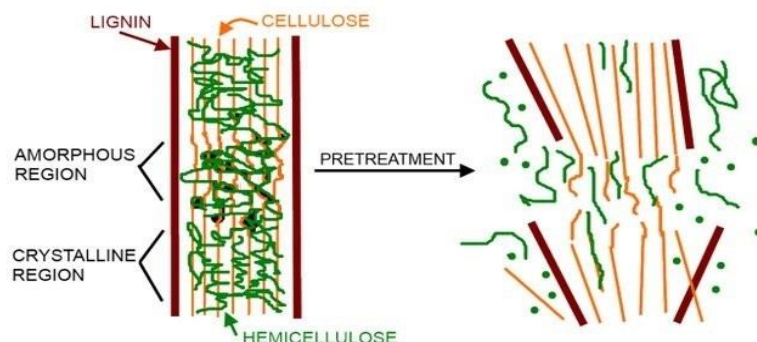
#### 3.1. Alkaline pre-treatment of lignocellulosic biomass

Lignocellulose feedstocks are mainly composed of cellulose, hemicellulose and lignin in various percentages depending on the source as shown in Table 1. There are also minor amounts of water, proteins and minerals present in lignocellulose structure. However, lignin is polymer of aromatic compounds which forms a protective layer for the plant walls while hemicellulose is a copolymer of different C5 and C6 sugars that also exist in the plant cell



wall and binds the cellulose structure together (Fig. 4). The presence of lignin impedes separation of wood into its component fibers; thus, delignification is a necessary step to obtain nanocrystalline cellulose. Some reviews

reported by Brodeur et al. [53], Kumar et al., [54] have been done on the various chemical pre-treatments available for lignocellulosic biomass.



**Fig. 4: Schematic representation of lignocellulose structure on pre-treatment [55]**

Wood and plant source materials undergo pre-treatment techniques which are similar to those used in the pulp and paper industry. Alkaline pre-treatment involves the use of hydroxyl derivatives of sodium, potassium, calcium and ammonium with sodium hydroxide being the most effective [56]. They act by degrading the side chains of esters and glycosides present in lignocellulose and this leads to structural modification of lignin, cellulose swelling, cellulose decrystallization and hemicellulose solvation [57-58]. It can then be inferred that alkaline pre-treatment is not a harsh treatment but requires moderate reaction conditions. This may involve a high temperature at a reduced time interval and vice versa. This treatment involves immersing the biomass in alkaline solutions and mixing it at a target temperature for a certain amount of time.

Cellulose pulps obtained from alkaline treatment are normally subjected to some other chemical pre-treatments like bleaching before acid hydrolysis. This next step of treatment (bleaching) is done in order to break down chromophoric groups present in the fiber. The bleaching treatment involves repeated soaking of the fibers in acetate buffer and sodium chlorite ( $\text{NaClO}_2$ ) followed by washing in distilled water. Washing and filtration using distilled water is conducted repeatedly on every stage of soaking in chemicals. The decolourized materials are broken down in water and the resulting suspension subjected to hydrolysis with acid treatment upon non-cellulose

constituent removal like lignin, pectins and hemicelluloses [70].

### **3.2 Acid Hydrolysis of Pre-treated Lignocellulosic Biomasses**

Acid hydrolysis is the process of breaking down the rigid lignocellulosic mass. However, acidic pretreatment or hemicellulose hydrolysis, involves the use of acid or hot water conditions to break down the primary cell wall to expose the underlying cellulose, hemicellulose and lignin. The removal of the hemicellulose and lignin is generally done by an acid or base due to its cost effectiveness [71]. The hydronium ion breaks down and attacks the intermolecular and intramolecular bonds among the cellulose, hemicellulose and lignin [72]. The degradation of cellulose when treated with acid begins with the accessible parts of the fibers, followed by reducing end groups then the crystal surfaces [51]. Reports suggest that diluted acids in appropriate temperature parameters are known to effectively remove hemicellulose, increasing the cellulosic yield. However, further treatment procedures, such as bleaching or chemical pulping, are undergone to release the encased cellulose. Hydrolysis techniques or an activation method tend to remove the amorphous regions, producing glucose monomers [10]. The acid specifically targets the amorphous regions, due to the disorder and voids present, whereas the more ordered regions tend to lack these voids [73].

**Table 1: Reaction conditions of various alkaline pre-treatment of lignocellulose biomass**

Lignocellulose	Alkali	Reaction Conditions				Results Obtained	References
		Time	Temp	Conc.	S/L ratio		
Sugar beet pulp	NaOH	2 hr	80°C	0.5M	1:10	Transmission light microscopy shows that sugar beet cellulose size ranging from 50-200um was obtained	[59]
Oil palm empty fruit bunch and oil palm bunch	NaOH	30 min	150°C	10 wt%	1:5	Decrease in lignin content in the oil palm EFB and OPF from 25.83% to 13.61% and 30.92% to 19.23% respectively.	[60]
Kellar grass	NaOH	60 min	121°C	2.5 wt%	1:10	52% delignification was obtained	[61]
Sugarcane bagasse	KOH	30 min	121°C	10 wt%	1:7	Decrease in lignin content from 19-5% and hemicellulose from 29-14%	[62]
Switch grass	KOH	1 hour	121°C	2 wt%	1:10	55.6% lignin reduction	[63]
Sugar bagasse and filter mud	NaOH	30 min	100°C	1N	1:12	79% decrease in lignin content	[64]
Rice straw	Ca(OH) <sub>2</sub>	3 hr	95°C	10 wt%	1:10	27% delignification	[65]
	NaOH	3 hr	55°C	4 wt%	1:5	23.1% delignification	[51]
Poplar wood	KOH	4 hr	30°C	0.2M	1:10	28% lignin content and 65% LNC yield	[66]
Hydrothermal treated sweet sorghum bagasse	Ca(OH) <sub>2</sub>	100 min	121°C	10wt%	1:9	55% lignin removal and final residual hemicellulose varied from 8.45-11.87%	[67]
Rice husk	NaOH	30 min	120°C	12%(w/v)	1:15	80.47% delignification	[68]
Wheat straw	KOH	24 hr	20°C	50%(g/g)	1:10	Hemicellulose decreased from 27.9% to 20.5% and lignin decreased from 18.4-13%	[69]

Pan et al., [74] studied cellulose nanowhiskers isolated by acid hydrolysis and observed using Fourier Transmission Infrared Spectroscopy

(FT-IR) and X-ray photoelectron spectroscopy (XPS) that the intermolecular hydrogen bonds and glycosidic bond breakage occurred during

hydrolysis reaction of the microcrystalline cellulose. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), Hydrochloric acid (HCl), Hydrobromic acid (HBr) and Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) are all acids used for cellulose hydrolysis for CNC and CNF preparation. The time elapsed during hydrolysis (reaction time), the concentration of the acid and the reaction temperature are some of the important factors controlling hydrolysis.

Yu et al. [75] studied the preparation and characteristics of bamboo nanocrystalline cellulose using sulphuric acid at various concentrations of 42, 44, 46, 48, 50 and 52 wt. % at constant reaction temperature of  $50^\circ\text{C}$  and reaction time of 30 min. It was observed that the CNC yield increased with increasing acid concentration until a certain level (above 48 wt. %) were continual increase leads to total degradation. The effect of various hydrolysis times (10, 20, 30, 40 and 50 min) at constant temperature of  $50^\circ\text{C}$  and at sulphuric acid concentration of 48 wt. % was also reported to exhibit little increase in yield with increased time of hydrolysis. Various materials like agricultural waste have been used in the preparation of CNC. Such studies carried out by Wulandari et al. [76] isolated CNC from sugar bagasse using sulphuric acid at 50 % and  $40^\circ\text{C}$  for 10 min. The nanocellulose was characterised using X-ray diffraction and the CNC showed high degree of crystallinity. Lee et al. [77] studied the use of hydrobromic acid (HBr) in preparation of CNC and its use in PVA composites. The CNC was prepared by adding 40ml/g 1.5-2.5M hydrobromic acid to micro crystalline cellulose at  $100^\circ\text{C}$  for 4 hr. The HBr treated CNC showed a higher thermal stability for the CNC.

The effect of four acids; sulphuric acid, hydrochloric acid, phosphoric acid and a mixture of acetic and nitric acid (ratio 10:1) was carried out by Zhang et al. [78]. It was noticed that sulphuric acid gave the highest crystallinity index followed by phosphoric acid. Hydrochloric acid and the mixture of acetic and nitric acid gave the lowest crystallinity index and they facilitate breakage of the hydrogen bonds in the crystalline region due to their capability to swell the cellulose. Among all these acids, sulphuric acid is the most commonly used acid for nanocellulose preparation; it produces a CNC with surface charge and stable colloidal dispersion when compared with other acids. Jeong et al. [79] studied the surface charge of cellulose nanowhiskers hydrolyzed using sulphuric and hydrochloric acids. It was

observed that sulphuric acid treated cellulose had surface charge within the range of 140.00 and 197.78 mmol/kg due to the presence of sulphate groups while in the HCl treated samples, no surface charge was detected. Though sulphuric acid hydrolyzed nanocellulose has more surface charge while HCl hydrolysed nanocellulose is more thermally stable.

Ren et al. [80] studied the effect of chemical treatment on the morphology and thermal stability of cellulose nanoparticles. The CNC were obtained from microcrystalline cellulose through the acid hydrolysis with sulphuric acid, hydrochloric acid and high-pressure homogenization. It was observed that though CNC treated with sulphuric acid has more surface charge, HCl treated CNC was more thermally stable. Since CNC produced using HCl or HBr has no surface charge, their colloidal dispersions were not as stable as CNC produced using sulphuric acid. Angellier, Putaux, Molina-Boisseau et al. [81] compared waxy maize starch on softwood kraft pulp hydrolyzed using sulphuric acid and hydrochloric acid. It was observed that CNC from HCl has a higher risk of agglomeration in aqueous medium but the charged group on CNC from sulphuric acid limits their ability to flocculate. Though CNC from HCl and HBr have no surface charge, they could be modified to achieve this. The lignocellulosic structure is represented in Fig. 5.

### 3.3 Enzymatic Hydrolysis of Nanocellulose

Enzymatic hydrolysis is an appropriate alternative when the corrosiveness, toxicity and environmental effect of acid hydrolysis are put into consideration. Cellulose nanocrystals can be obtained through this process and it is carried out using cellulases [36]. Similar to acid hydrolysis, enzymatic hydrolysis involves the alteration of the cellulose amorphous region of the cellulose while conserving the crystalline region [36].

Tang et al. [83] combined enzymatic hydrolysis, acid hydrolysis and sonication process to produce CNC from old corrugated pulp fiber containers. The result revealed a CNC yield of 13.3% without enzymatic treatment, whereas an increased yield was obtained after hydrolysis with enzymatic treatment. That is to say that, the presence of enzymes increased the crystallinity, though, yield of CNC and thermal stability was also observed. Two different methods of enzymatic hydrolysis of nanocellulose were reported which are direct

and indirect enzyme modifications [84]. However, the study showed that the enzymatic method of nanocellulose production and functionalization is a feasible ecological modification strategy compared to chemical modification approach. The most frequently used classes of enzymes are hydrolases and oxidoreductases, with lipases, proteases and glycosidases being the commonly used

hydrolase enzymes, whereas peroxidase, tyrosinase and laccase are the mostly utilized oxidoreductases enzymes. Although enzymatic hydrolysis of nanocellulose offers higher yield, higher selectivity, lower energy cost and milder operating conditions than chemical processes. However, this is still hindered by high cost of cellulose enzymes and long processing period [85-86].

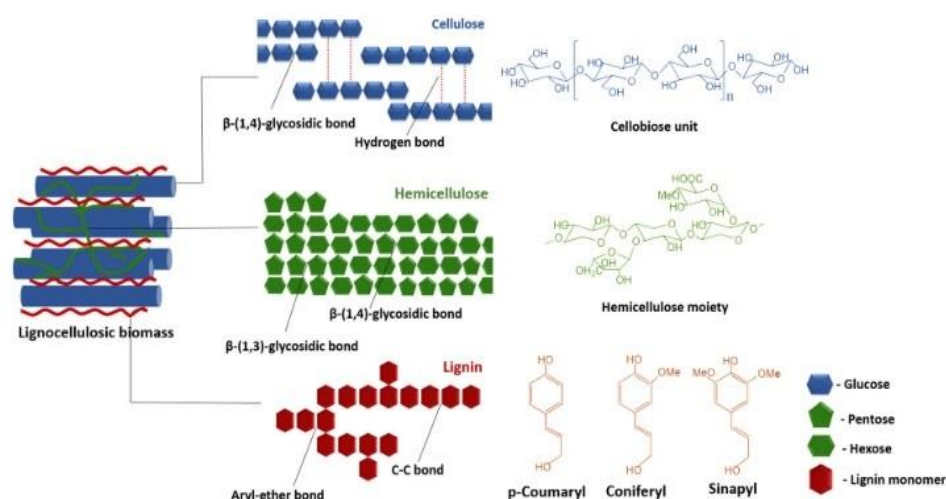


Fig. 5: Schematic representation of lignocellulose [82]

Ahola et al. [87] reported that a detailed knowledge of surface chemistry of cellulose and specific interaction between the enzyme and cellulose is needed for economically viable transformation of cellulose through enzymatic processes. Nanocellulosic materials functionalized through enzymatic approach are non-toxic, which is a significant advantage over their chemical method counterpart and can best be employed in biomedical applications [88]. It is worthy of note that application of bacterial cellulose in engineering operation is an emergent subject of concentration amid materials scientists and engineering [89]. For example, Akhlaghi et al. [90] studied the vulnerability of bacterial nanocellulosic fiber reinforced cement composites, in which bacteria nanocellulose was reported to improve the cement mortar's mechanical behaviours. Accordingly, advancement in nanocellulose layers functionalization possessing complete surface properties by means of viability, remains a tough venture in nanocellulose investigation.

### 3.4. Chemical modification of nanocellulose

Nanocellulose (NC) contains a number of crystalline regions due to their linear and conformationally homogeneous nature and the broad intermolecular hydrogen bonding between adjacent cellulosic chains. The extent of crystallinity and size of the crystalline regions depend on the natural source of the cellulose and the isolation approach [91]. Functionalization of nanocellulosic materials has attracted a great number of researchers due to tremendous improved properties and characteristics they possess, qualifying them to be applied in the area of material science as value-added materials. Cellulose is a natural carbohydrate and biopolymer, which is abundant and functions as a major constituent in structural hierarchy [92]. Nanocellulose have been used extensively as polymer nanocomposite's reinforcements [93-97]. The ability of nanofillers to disperse efficiently in the matrix and adequately interact interfacially within the nanofiller-matrix is usually known to have significant influence on material's physical and mechanical properties. Attainment of excellent distribution of nanocellulose reinforced polymer matrices in water-insoluble or non-water soluble is challenging, due to its



characteristic hydrophilicity. This restraint emanates basically from its high affinity for water in addition to the inability to willingly disseminate in organic solvents. Apparently, cellulose nanoparticles are defined by hydrogen bonding driven combination enhancement as a result of their nanosized and fibrillar structures. On account of OH groups present on the surface of nanocellulose resulting from their massively hydrophilic nature, their surface chemistry could be modified by chemical, physical interactions [98] and biological strategies. However, hydrophobic compounds with covalent and non-covalent coupling approaches can also be employed for cellulose nanoparticles surface functionalization in order to prevent it from stiffening and boost effective distribution in non-aqueous media. Apart from difficulty in homogeneity with polymer matrices, enhanced nanofiller-matrix correlation is anticipated to improve stress transference from the polymer matrix to the homogenized section and at the same time, advance the material's load-bearing capacity. Besides, nanocellulose with specific functionality might be attained through nanoparticle surface design. Surface functionalization of nanocellulose can be performed in the course of preparation stage or post-production stage [99]. These modifications give rise to attainment of desired performances, and subsequently, improve their efficiency for any specified application [100-103]. However, integration of chemical functionalities on the surface of nanocellulose leads to chemical modification in which the material may react with strange materials [104]. Literature have it that the surface of nanocellulose, in addition to physical and enzymatic approaches, can be chemically modified employing several approaches, mostly covalent surface functionalization which include esterification, cationization, sulfonation, polymer grafting, nucleophilic substitution, etherification, silylation, carbamination, carboamination, TEMPO-mediated oxidation and non-covalent surface chemical modification among others [104, 101, 105, 98, 19, 70]. Though, chemical modification methods such as coupling of hydrophobic small molecules and adsorption of hydrophobic compounds to surface hydroxyl groups of cellulose nanoparticles, may likewise apply. CNC surfaces can be modified by surface adsorption of molecules or macromolecules or by physical interaction, which could be, either by adsorption of surfactants or adsorption of macromolecules [70]. Figure 6 presents

illustrations of most frequently applied surface modification approaches of nanocellulose.

Improved thermal and mechanical properties of nanocellulose reinforced polymers were achieved through surface functionalization of polysaccharide nanocrystals [92]. Conversely, CNC apart from being made up of hydroxyl groups primarily possesses significant surface area to volume ratio, which makes them extremely reactive and easily functionalized. Chemical modification of cellulose nanocrystals introduces steady electrostatic charges on their surfaces which enhances their compatibility and better the distribution of their particles [106].

Lu et al. [107] investigated PLA's hydrophobic reduction through interfacial compatibility of hydroxyapatite modified nanocellulose/PLA. TEM, FT-IR and X-ray diffraction analysis confirmed effective structural modification of cotton pulp derived-nanocellulose. The study reported improved mechanical properties of PLA nanocomposite attributed to uniform dispersion of the nanocellulose and presence of strong hydrogen bond relation at the interface as seen in the fabricated films. In addition, improved tensile strength, modulus and thermal stability was also reported to have resulted from the surface functionalization, hence, significance of better reinforcing ability exhibited by the nanocellulose.

#### **3.4.1. Chemical modification of cellulose nanocrystals during acid hydrolysis**

Cellulose nanocrystals (CNC) demonstrate high surface area owing to their nanoscale dimensions and virtually any surface functionality could be introduced to them on account of their surface hydroxyl groups [109]. CNC can be modified simultaneously through hydrolysis approach in a chemical synthesis under acidic conditions, in the presence of water. However, as reported in the literature, CNC surface chemistry depends on the acid utilized during hydrolysis. Cellulose nanocrystals prepared using sulphuric acid hydrolysis activate sulphate ester groups on the surface of the CNC. More so, the density of these sulfate groups has also been reported to increase with acid concentration, time and temperature [110]. Hydrolysis with acids such as hydrochloric acid (HCl) and hydrobromic acid (HBr) have been reported to maintain hydroxyl groups of the native cellulose which results in an unsteady suspension [111]. Several

studies on different types of CNC modifications have been reported owing to the abundance of the hydroxyl groups at the surface of CNC [19, 112, 109]. All chemical modifications are investigated primarily to introduce stable

electrostatic charges on the surface of CNC for enhanced distribution or to improve compatibility coherence of CNC, by fine tuning its surface energy characteristics [19].

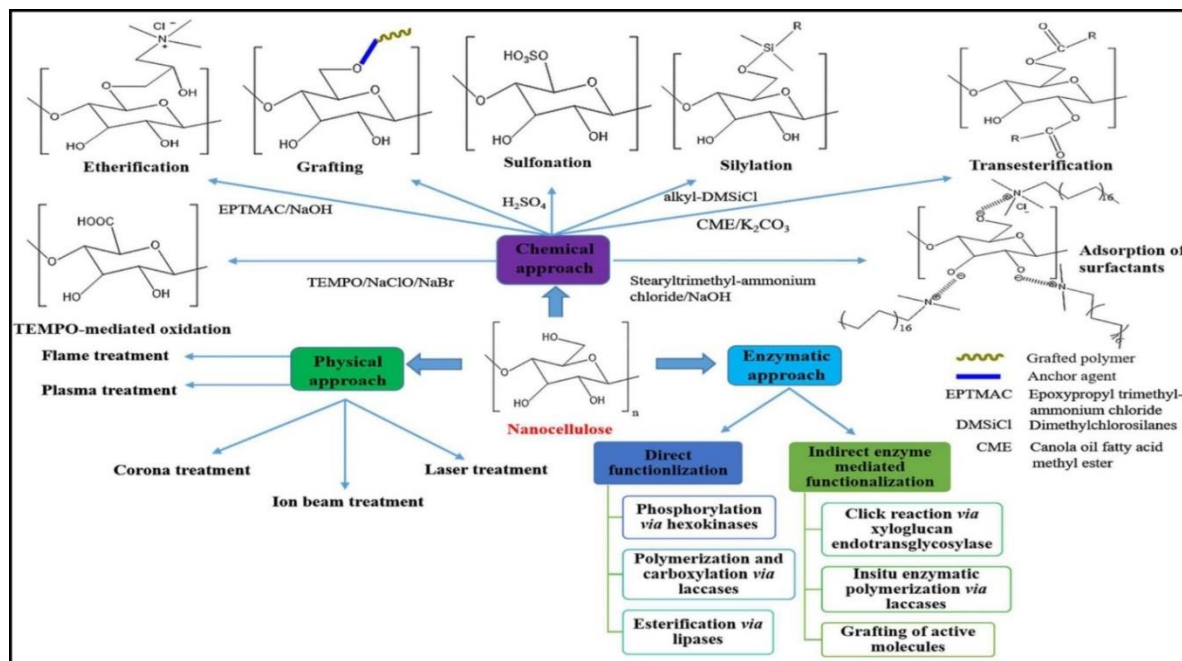


Fig. 6: Schematic illustration of most frequently applied surface modification approaches of nanocellulose [108]

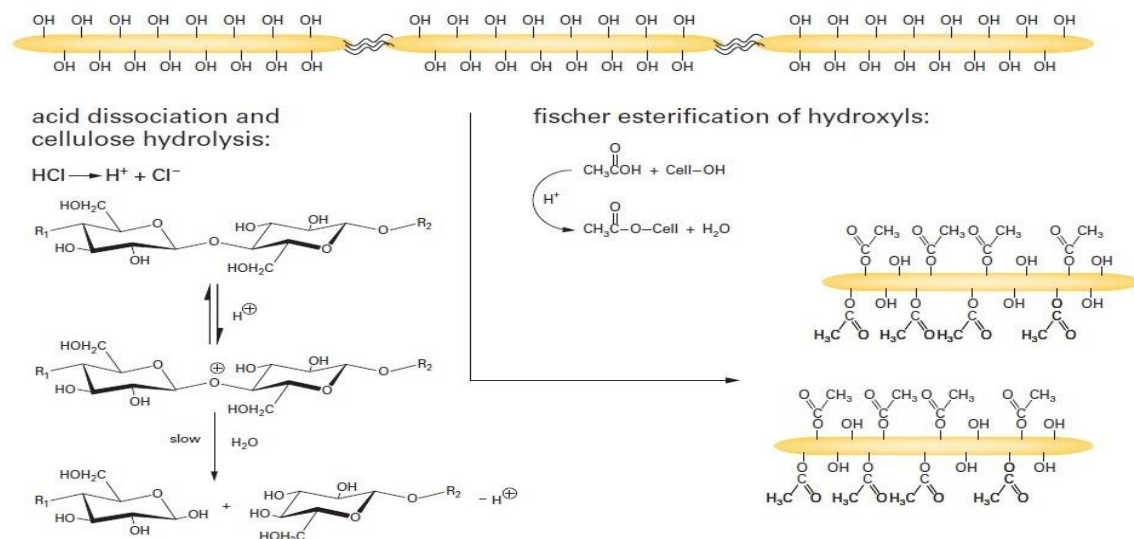
One major challenge of chemical modification of CNC is the ability to carry out the chemical modifications in a way that it only alters the surface of the CNC while the morphology and integrity of the crystals are still maintained. A better alternative to this method is Fischer esterification reaction approach, which comprises refluxing of a carboxylic acid with an alcohol in the presence of an acid catalyst. Reports on CNC modifications during hydrolysis are limited; however, this hydrolytic modification is important for cellulose-polymer matrix interfacial enhancement in biocomposites [113]. Acid hydrolysis with sulphuric acid could be regarded as simultaneous hydrolysis and modification, due to the sulphate groups attached to the CNC surfaces [113]. Simultaneous hydrolysis and acetylation of CNC with HCl mixture, butyric and acetic acids was reported [114]. During the hydrolytic process, amorphous cellulose was broken down and the resulting CNC was modified via Fischer esterification method of hydroxyl groups as seen in Figure 7. The process revealed that a greater percentage of

the hydroxyl groups were modified. Yan et al. [115] reported a study on the surface modification of CNC from cotton fiber by single step method. In this method, polyphosphoric acid and 85% phosphoric acid were mixed to prepare anhydrous phosphoric acid system which was later mixed with acetic anhydride. The phosphoric acid hydrolyzes the fiber and the CNC was also acetylated in a single step procedure.

From a theoretical point of view, two ways to achieve simultaneous hydrolysis and modification is by finding an acid that hydrolyzes cellulose fibers and modifies the CNC or addition of a reagent to the acid used for hydrolysis, which could react with the nanocrystal and at the same time, remain functional in the acidic and aqueous conditions [113]. Heravi et al. [116] reported a review on successful attempt to convert cellulose into glucose, using water at 190 °C, zeolite, sulphate, zirconia supported over mesoporous silica, amberlyst-15 and a heteropoly catalyst. However, results revealed that environmentally

harmful liquid acid catalysts could be replaced with heteropoly acids, a solid promising green acid catalyst. A number of CNC reforms might be considered more effective in diverse conditions.

For instance, modification with isocyanate was reported to improve its dispersion with the polyurethane system [117].



**Fig. 7: Instantaneous reaction scheme of cellulose hydrolysis and Fischer esterification process with acetic and hydrochloric acids mixtures [114]**

### 3.5. Surfactant Adsorption

Utilization of surfactant adsorbents [118] and polymer coatings [119] for nanocellulose fictionalization has been in practice since time immemorial. Compounds containing both hydrophobic tails and hydrophilic heads (surfactants) have been used as stabilizing agents to modify the surface of CNC [120]. A surfactant molecule contains both oil and water-soluble constituents. However, the hydrophilic head of the molecule might absorb the CNC surface while the hydrophobic tail extends out, lowering the surface tension of CNC [70]. Surfactants consisting of monoesters and diesters of phosphoric acid bearing alkylphenol tails have been reported [120]. The resultant surfactant coated CNC was observed to disperse completely in non-polar solvents. In their work, they modified CNC via a non-covalent adsorption route. CNC extracted from cotton linters was modified using anionic surfactants comprising phosphate esters of ethoxylatednonylphenol [121]. Kim et al. [122] and Rojas et al. [123] reported successful adsorption on the use of non-ionic surfactant to disperse CNC in polystyrene based composite fibers. The study reports adsorption and network structure of nanocellulose at the fluid interface. Nanocellulose comprising native hydrophilic and hydrophobic surfaces was

observed to introduce various network structures and chemisorption attributes [124]. It is worthy of note that nanocellulose is a green alternative to fluid interface stabilization. The adsorption of nanocellulose in the oil-water interface speeds up the creation of Pickering emulsions that are steady and biocompatible. In addition, the study revealed that unmodified nanocellulose could not stabilize foams. Conversely, nanocellulose with covalent surface modifications or adsorption of surfactants might hydrophobize its surface with contact angle,  $\theta > 90^\circ$ , and subsequently, stabilized foams. In relation to nanocellulose excellent stability and compatibility, many innovators utilize nanocellulose-stabilized colloids, for example, preparation of 3D-printing inks [125-126], unique nano-biocomposites [127-128], and gastric firm distribution schemes [129-130].

Investigation on the equilibrium of concentrated consumable oil-in-water Pickering emulsions through CNC surface modification with ethyl lauroylarginate was reported [131]. Results from this study revealed that the more hydrophobic the surfactant enclosed nanocellulose becomes, the lower the surface tension on the CNC surface and the higher the surface expansion, adding to improved electrostatic equilibrium and emulsifying

competency. Most physical surface functionalization strategies employed might comprise of electric discharge (plasma treatment), ultrasonic treatment, irradiation and surface fibrillation [119]. Cellulose nanofibrils exhibit unique characteristic superior bulk and interfacial elasticity enabling spreadability into bulk, which results in formation of more stable foams when compared to CNC [132].

### 3.6. Cationization

Positive charges can be introduced to the surface of nanocellulose to aid surface modification. Epoxy propyl trimethylammonium chloride (EPTMAC) containing weak or strong ammonium groups were successfully grafted onto the CNC surface [133]. However, a nucleophilic incorporation of alkali-activated cellulose hydroxyl groups of epoxy moiety of EPTMAC was employed for surface cationization, which resulted to a stable aqueous suspension of CNC with unexpected thixotropic gelling properties. This report records absence of liquid crystalline chiral nematic phase separation due to high viscosity of the suspension, however, absence of shear birefringence was also observed.

### 3.7. Esterification and Acetylation

The surface modification of cellulose has often been attained due to the ability of cellulose to undergo esterification reaction. Acid anhydrides and acyl chlorides are the basic acetylating agents employed for this purpose which incorporates acetyl functional group ( $\text{COCH}_3$ ) within the cellulose surface. However, esterification reaction introduces ester functional groups ( $\text{COO}$ ) on the surface of nanocellulose through carboxylic acid group condensation [70].

Mixture of acetic acid and anhydride was utilized to modify the structure of CNCs from valonia and tunicates through acetylation [134]. In the reaction process, toluene was used to terminate swelling and dissolution of cellulose acetate. Diffraction and TEM results reported, revealed limited decrease in CNC length while as the reaction preceded, a decrease in diameter of the crystals was observed. It was noted that upon acetylation, nanocrystals did not break down longitudinally but rather, laterally. In heterogeneous acetylation, cellulose acetate surrounds the crystalline center of unreacted

cellulose and remains insoluble, while in homogeneous conditions; the partially acetylated molecules partition themselves into acetylating medium and become soluble. The hydrophobic properties of CNC extracted from tunicin have been improved with the use of alkynyl succinic anhydride (ASA) [135]. Surface acetylation of CNC by transesterification of vinyl acetate with potassium carbonate was reported to destroy the crystalline structure of the CNC as the reaction time increases. However, as acetylation proceeds, stability of the nanocrystals in tetrahydrofuran (THF) was achieved [136]. Apparently, the esterification of CNC extracted from ramie with different aliphatic chain length of fatty acid chlorides under reflux, resulted in CNC with crystalline core that is unaffected. As well, utilization of 18 carbon atoms and crystallization of grafted chains brought about unaffected crystalline core due to the presence of high enough grafted atoms [137]. An example of esterification reaction is elucidated in Fig 7.

### 3.8. Silylation

Silylation involves addition of substituted silyl groups ( $\text{R}_3\text{Si}$ ) on nanocellulose surface, Figure 8a. This process has been considered an effective way to improve the properties of nanocellulose. In the last decade, there have been remarkable studies on silylation modifications of nanocellulose [138-139]. The utilization of iso-cyanate propyl triethoxysilane (IPTS) for silylation modification has been reported to affect only the nanocrystal surface of CNC protecting the cellulose structure, Figure 8b. However, high IPTS contents displayed good dispersion, due to more triethoxysilane moieties onto the nanocrystal surface. A strong Si energy peak was seen in the Silylated CNC (SCNC), which indicated successful silylation of CNC, Figure 9. Additionally, the intensity of Si peak was progressively increased as IPTS contents were increased, and this further confirmed more interfacial bonding of triethoxysilane moieties onto SCNC surface [138]. Goussé et al. [140] reported a study on the partial silylation of CNC extracted from tunicin involving a series of alkyl dimethylchlorosilanes, ranging from short carbon length of isopropyl to longer carbon length of n-butyl, n-octyl and n-dodecyl. It was reported that the CNC became dispersible in low polarity solvent such as tetrahydrofuran with a surface degree of substitution (DS) of the



order 0.6-1, keeping their morphological integrity intact. Although at increased silylation (DS greater than 1) breakage of the crystals and loss of initial morphology as a result of the silylation of the chains in the core of the catalyst was observed. CNC extracted from cotton was functionalized by partial silylation through

reaction with n-dodecyldimethylchlorosilane, while homogeneous dispersion in PLA was obtained with increased rate of crystallization of the matrix [141]. Silylated modification of CNC extracted from ramie was also reported to be compatible with PLA [142].

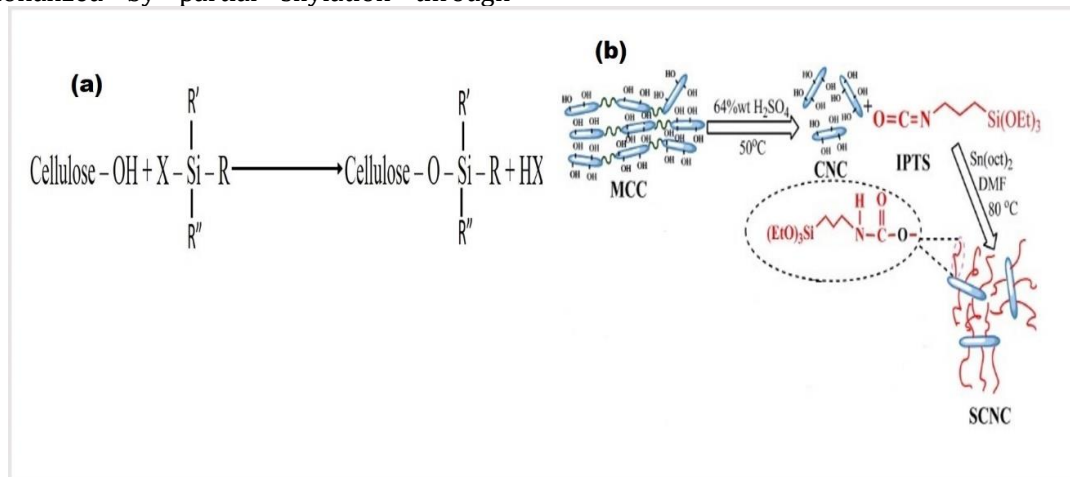


Fig. 8 (a) Silylation of cellulose (b) Synthesis route of silylation modification of CNC (SCNC) [138]

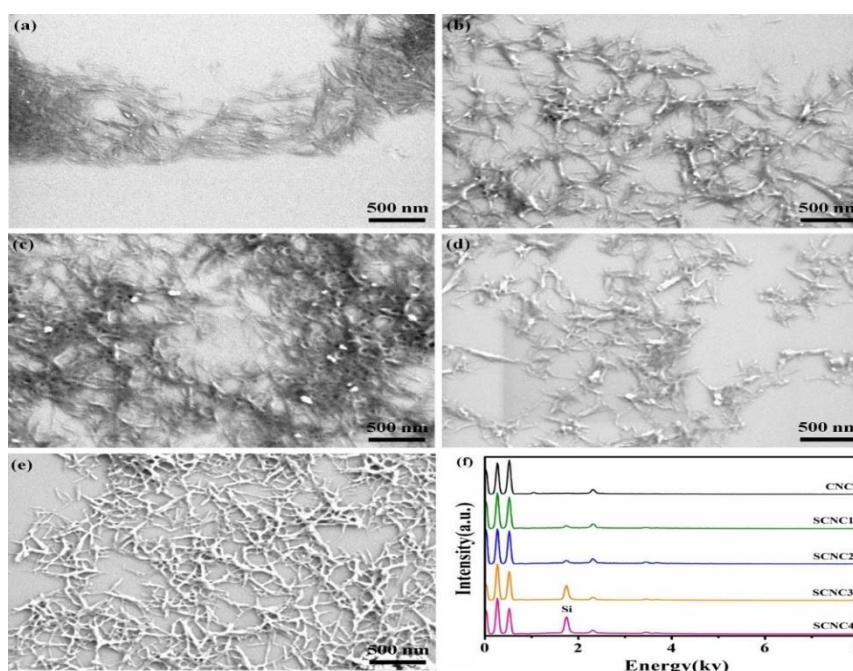


Fig. 9: FE-SEM images of (a) CNC (b) 0.1 wt. % SCNC (c) 0.2 wt. % SCNC (d) 0.3 wt. % SCNC3 (e) 0.4 wt. % SCNC4 and (f) SEM- EDS of CNC and SCNC samples [138]

Fig. 9(a) depicts unmodified CNC with rod-like structure of about 5–30 nm diameter and 200–300 nm length. Figure 9(b–e) represents CNC with SCNC contents ranging from 0.1 – 0.4 wt. %, indicating no significant changes in the structures of the SCNC with varying IPTS/CNC contents. This indicates that chemical modification occurred, as desired, only at the

nanocrystal surface, conserving the cellulose structure. As well, the SCNC with high IPTS/CNC content (0.4) was observed to exhibit good dispersion, attributed to added triethoxysilane moieties onto the nanocrystal surface.

### 3.9. Carbamation

*Iheoma Chigoziri Nwuzor et al.,*

Carbamation involves the use of isocyanate to modify nanocellulose. It can be grouped into either tolylene-2,4-diisocyanate (TDI) or non-polar isocyanate for surface modification of CNC [143]. The approach for isocyanates is to a certain extent related to the silane coupling agent approach, by which the hydroxyl group is the point of interconnection for the functionalization reaction with oxygen at the end of the functional group. This forms a urethane chain grafted onto the surface of the CNC. Habibi and Dufresne [144] reported the modification of CNC by grafting polycaprolactone (PCL) to CNC with TDI using triethylamine as catalyst at reaction time of 7 days and temperature of 90 °C. Similarly, Zoppe et al. [145] reported the same reaction but with a shorter reaction time of 24 hr. However, neither of the studies reported the degree of substitution due to the modification. On the other hand, Siqueira et al. [146] reported a study on the modification of CNC extracted from sisal using n-octadecyl isocyanate without a catalyst, yet, achieved a degree of substitution (DS) of 0.07.

CNC surface modification with isophoronediiisocyanate (IPDI), in which CNC was dispersed in dimethyl sulfoxide (DMSO) via sonication prior to mixing with IPDI and a catalyst was reported [117]. The reaction of the product was performed in a nitrogen environment at 60 °C for 24hr utilizing polarized light microscopy. The functionalized CNC exhibited improved dispersion within the polyurethane matrix unlike the unmodified CNC. CNC modification using n-octadecyl isocyanate was reported by Siqueira et al. [147]. Both methods depend on a solvent exchange with acetone as the initial material and afterwards diverged to dichloromethane and then finally to toluene. The second solvent relied on an in-situ solvent exchange for the acetone to toluene instead. Through the solvent exchange to toluene, an additional amount of noctadecyl isocyanate was introduced dropwise and thereafter, heated to 110 °C. From their study, the first method exhibited uneven distribution compared to the second process which was seen to be uniformly homogeneous within the polymer film, indicating a better effective modification mechanism.

### 3.10. TEMPO-Mediated Oxidation

TEMPO-mediated oxidation is one of the major approaches explored lately for

nanocellulose functionalization. TEMPO oxidation is an oxidizing agent frequently utilized for the conversion of alcohols to aldehydes, and at the same time, for carboxylates and ketones productions. This approach is usually performed with sodium hypochlorite and sodium bromide, which oxidizes the hydroxyl groups existing on the surface of the cellulose fibres to carboxylate groups [148]. From conductometric titrations, it was shown that the oxidation of the cellulose increased with increase in the concentration of sodium hypochlorite. Change in oxidation was not observed to significantly influence the material's crystallinity. The whole approach was best performed on individual nanofibrils for the establishment of a simple one-pot production of modified nanocellulose. TEMPO-mediated oxidation approach is usually employed as a precursor form of modification prior to further functionalization like polymer grafting [149].

The conversion of hydroxymethyl groups on the surface of CNC into carboxylic form was reported to be possible using 2,2,6,6-tetramethylpiperidine-1-oxy mediated (TEMPO-mediated) oxidation [19]. Araki et al. [150] modified CNC obtained from acid hydrolysis with HCl and reported that the morphological integrity of the modified CNC was maintained alongside formation of uniform mixture of the CNC with water, after the TEMPO-mediated oxidation. The ability to form homogeneous suspension was reported to be due to induced electrostatic stabilization resulting from the carboxylic groups which conveyed negative charges on the CNC. Ferreira et al. [151] also made similar observations after modifying CNC employing the TEMPO-mediated oxidation. The studies also reported reduction in crystal size during excessive TEMPO-mediated oxidation which resulted from the partial separation of cellulose chains present on the surface. Habibi et al. [152] studied the TEMPO-mediated oxidation of CNC extracted from tunicates with HCl and reported sustained crystallinity and morphology. When dispersed in water, the TEMPO-mediated CNC suspensions were observed not to flocculate or sediment as a result of the negative charge on their surfaces [19].

The TEMPO-mediated oxidation reaction scheme in Figure 10 comprises TEMPO/Sodium bromide (NaBr)/Sodium hypochlorite (NaClO) in water, with pH of 10-11. This is anticipated to

transform C6 primary hydroxyls of cellulose to their carboxylate groups. In this process, NaClO was introduced to aqueous suspension of cellulose with catalysts, thereafter; TEMPO and NaBr were added at room temperature. The aldehyde groups converted the C6 primary hydroxyl groups of the cellulose to carboxylated

groups, with only NaClO and NaOH being absorbed [154]. Part of the hydroxymethyl groups were available for reaction while the remaining part were obtainable due to the presence of a 2-fold screw axis exhibited by the cellulose chain [152].

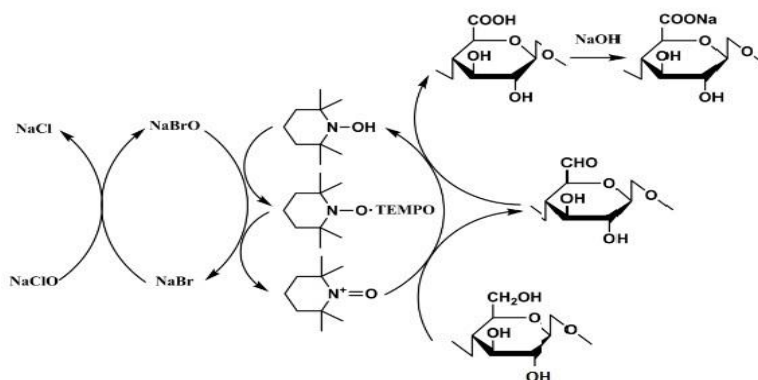


Fig. 10: The reaction structure of cellulose TEMPO-mediated oxidation [153]

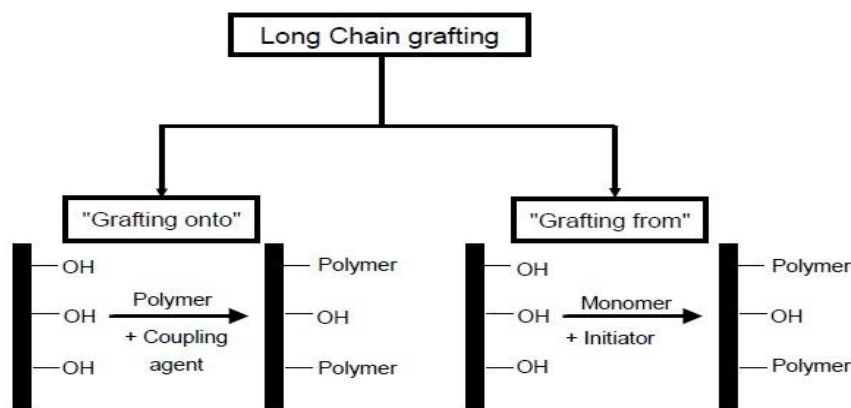
### 3.11. Grafting of Polymer

Grafting of polymers upon nanocellulose surfaces has been explored employing several approaches. Two main methods commonly employed for grafting of polymer on CNC surfaces are “grafting onto” and “grafting from” [155]. In the grafting onto, polymers are attached onto the hydroxyl groups at the surface of the cellulose by means of coupling agent whereas in grafting from, the polymer chains are developed by in situ surface-initiated polymerization from immobilized originators on the substrate as seen in Figure 11.

Malleated polypropylene was grafted onto the surface of CNC isolated from tunicates and the result revealed excellent compatibility and high adhesion when dispersed in atactic polypropylene [156]. Habibi et al. [157] reported acid hydrolysis of CNC, reacted with isocyanate-mediated and grafted onto polycaprolactone (PCL) chains with several molecular weights on their surface. The grafted PCL chains were reported to crystallize at the surface of the CNC due to high enough grafting density. Araki et al. [150] reported a study on the grafting of an amine terminated polymer onto the surface of CNC prepared with HCl employing a caboxylated-amidation approach. A dried grafted CNC re-dispersed in water/non-aqueous solvents was achieved together with better dispersion stability upon inclusion of sodium chloride. Kloser and Gray [158] grafted

aqueous suspensions of polyethylene oxide on CNC extracted from cotton and reported greater steric behaviours rather than electrostatic stabilization.

Polyacrylamide grafted onto CNC was incorporated into poly (vinyl alcohol) (PVA) through solution casting process for nanocomposite films reinforcement [159]. Result revealed improved interfacial homogeneity confirmed by the presence of firm hydrogen bonds formed on CNC surface which was between hydroxyl groups of PVA matrix and polyacrylamide chains, through infrared spectroscopy. Increased elastic modulus of the nanocomposite was achieved at 0 and 50 % relative humidity. CNC surface modification through grafting significantly improved the thermal stability and mechanical properties of the PVA-nanocomposites. Conversion of cellulose nanofibrils into hydrophobic material through cinnamoyl chloride and butyryl chloride grafting was reported to exhibit satisfactory surface properties, competent enough to stabilize oil-water emulsions [160]. However, the authors reported the inability of nanocellulose possessing greater surface charge density to successfully stabilize Pickering emulsions, and this, in any case, restricted their utilization as interfacial stabilizers. Hence, surface functionalization through hydrophobic polymer grafting on nanocellulose, improves their wettability through the oil phase and results in interfacial tension reduction.



**Fig. 11: The schematic illustration of polymer grafting (onto and from) approaches [112].**

A typical polymer grafting approach based on atom transfer radical polymerization (ATRP) has been in practice which allows for in-situ polymerization methods. Methyl methacrylate (MMA) and butyl acrylate (BA) are two major monomers grafted onto CNC [161]. For the atom transfer radical polymerization (ATRP) reaction to take place, the CNC surface was initially bound to an originator configured with 2-bromoisobutyl bromide. The in-situ polymerization developed among the bromide groups was bound to the surface with MMA and BA in solution. Graft copolymerization process using MMA through CNC dispersion in ceric ammonium nitrate/nitric acid solution which contains MMA was reported [162]. The solution was allowed to copolymerize for 3 hr. at 45 °C with successful grafting recorded. Surface functionalization of polysaccharide nanocrystals through free radical polymerization was reported to record success, promoted by ozone (ozonolysis) which broke the double bonds in the organic chains to generate new reaction sites [163]. Subsequent upon ozonolysis, an additional reagent might be introduced to allow for complete modification. The study revealed improved CNC's thermal stability of approximately 100°C post modification. However, the study suggests advancement in the hydrophilic property reduction to boost the efficiency of the grafting approach. Grafting of poly(ethylene oxide) (PEO) onto the CNC surface in an aqueous suspension was reported by Kloser & Gray [164]. This approach of polymer grafting involved incorporation of epoxy terminated PEO into a solution of sodium hydroxide and CNC, followed by heating for a period of time prior to dialysis to eliminate extra materials that might remain. Report revealed that the CNC maintained stability within the solution upon modification.

Research and studies have been carried out using the grafting “from” approach of cellulose modification. For example, Habibi et al. [157] used ring opening polymerization with stannous octoate as the grafting and polymerizing agent respectively, to graft polycaprolactone on the surface of CNC. The morphological and structural integrity of CNC was seen not to be affected after the polycaprolactone grafting of the CNC. Cao et al. [165] researched on the one-pot polymerization; processing and surface grafting of CNC reinforced waterborne polyurethane (WPU) nanocomposites. WPU prepolymer was prepared using polycaprolactone diol and isophoronediiisocyanate through casting and evaporation approaches for nanocomposite fabrication. The chains upon grafting were observed to develop into crystalline structures on the nanoparticles surface and consequently triggered crystallization on the polymer matrix. Yi et al. [166] grafted CNC with polystyrene using atom transfer radical polymerization (ATRP). 2-bromoisobutyryloxy groups were employed to activate the polymerization reaction of polystyrene. The synthesis was carried out via esterification. The polystyrene-grafted CNC was reported to exhibit chiral-nematic configuration in both thermotropic and lyotropic conditions. Morandi et al. [167] utilized surface-activated atom transfer radical polymerization to develop a range of polystyrene-grafted CNC, with varying grafted lengths and modified grafting density, through control of the final content of activating sites. Utilizing grafting from approach, the polymers were characterized before grafting but, however, present high steric hindrances.

### 3.12. Silane coupling agent's reactions



Utilization of coupling agents such as silane for modification of nanocellulose, is yet to be explored. The coupling agents in practice consist of reactions of oxy and hydroxyl groups existing on the nanocellulose surfaces, which however generates alcohol as a by-product. Silane, as coupling agents usually contains long chains that are beneficial for the reduction of hydrophilic properties of nanocellulose. One of the major benefits of using silane coupling agents is the ability to allow for additional adjustment on the grafted polymer chain which is dependent on the individual coupling agent used. A number of approaches with various silane agents have been investigated for nanocellulose modifications [168-170]. Kargarzadeh et al. [171] reported the utilization of N-( $\beta$ -aminoethyl)-aminopropyltrimethoxysilane (APS) for CNC surface modification. In their approach, CNC was dispersed in water and ethanol solution containing silane agent. The solution was sonicated for 3 min upon pH adjustment and allowed to relax for 2 hr. This approach is very easy to handle and hence, besides sonication, no additional energy is required to appropriately disperse the CNC within the water/ethanol solution, being a one-pot reaction. TEM analysis of the modified CNC revealed improved dispersion with less accumulation when blended with a polymer matrix in contrast to the initial CNC, demonstrating enhanced hydrophobic behaviour. An updated version of the above approach was employed with slight modification for 3 hr heating period at 60°C for elimination of excess silanes that remained in the solution [172]. Results also revealed improved surface modification.

De Oliveira et al. [139] utilized 3-isocyanatepropyltriethoxysilane (IPTS) as CNC surface modifying agent. A somewhat easy approach was employed for CNC dispersion in an inert nitrogen environment prior to reaction with a silane coupling agent for 8 hr. followed by addition of catalyst and mixing for an additional 30 min. The result of the optical microscopy revealed that the modified CNC showed enhanced uniform distribution within a non-polar solvent. Polylactic acid (PLA) and CNC crosslinking was studied employing vinyltrimethoxysilane, a vinyl-based silane coupling agent [173]. In this approach, the silane agent was first melted with PLA forming bonds with the vinyl groups in combination with the CNC suspension which was then heated

to form silanization, allowing bonding with the PLA. Result revealed homogeneous dispersion and improved bonding.

#### **4.0 Barrier properties of nanocellulosic films**

##### **4.1. Gas barrier properties**

The presence of oxygen barrier in food packaging is very vital as it helps the aerobic microorganisms in food damaging with decline in its nutritional worth. Low oxygen environment is essential to enable extension of the food shelf-life. Apparently, nanocellulose (NC) has the potential for hydrogen bonds formation (with itself in addition to with different biopolymers) which creates a solid network that hinders numerous gas molecules to pass across as a result of tiny pore size. Besides, the high crystalline regions present in nanocellulose are impenetrable to gases, turning it to a great material for gas barrier properties. The rate of gas permeability relies upon the disintegration of gas and its rate of dispersion in the packaged polymer films [174]. It is noteworthy that at a relative humidity (RH) extent of about 70%, the hydrogen bonds diminish the gas penetrability due to increased coherence [175-177]. Further increase in RH values led to diffusion of the moisture together with the gases in the surroundings within the polymer. It may therefore be deduced that atmospheric conditions are essential and should be considered during the time of designing materials for packaging applications.

Enhanced barrier properties in food packaging applications such as nuts, dried fruits, spices, etc, which necessitates less moisture content through multilayer packaging have been reported [178]. Cellulose nanofibrils (CNFs) coated on polyethylene terephthalate (PET) and further layered with low-density polyethylene (LDPE) through extrusion, results in configuration with three layers. The barrier behaviour of the reported multifaceted film compared favourably with the commercially viable ethylene vinyl alcohol multilayer barrier film. Increased CNF content (1 – 7 g/m<sup>2</sup>) coating on paper, results in decreased air penetration, in addition to oxygen penetrability (OP) of the paper by 70 and 104 % accordingly [179-180]. Paper coating is essential as it improves the barrier performance, tensile strength, oil and moisture resistance [181]. The use of CNF and condensed tannin as antioxidants for food packaging composite fabrication was reported [182]. Antioxidants alleviate the oxidation kinetics of food with and/or without oxygen.

The produced composite was reported to exhibit improved tensile properties, enhanced surface hydrophobicity in addition to high density which resulted to outstanding 6-fold upturn in barrier properties as regards air, in comparison with pure CNF film (19.27 mL/min) and 90-folds in comparison with normal A4 size paper (277.2 mL/min). The resistance to air was approximately 3.1 mL/min, a level which competes favourably with polypropylene-derived chocolate plastic packaging

However, in a study reported by Hubbe et al. [183], the composite film fabricated struggles to conquer the drawback of NC films, at which point the density of the film requires to be imperiled with a view to reduce the attraction with respect to water, in that way deteriorating the barrier properties. Literature has it that gas penetrability in CNC films is greater than those in CNF films [184]. The development of thick entanglement by CNF film complex structure was ascribed to lower penetration of gases by the system. It has been reported that CNF films exhibits oxygen transmission rate (OTR) of about 17 mL/m<sup>2</sup>/day [185-186], that is comparable to most petroleum-based polymers [187]. Fabrication of CNC/CNF/gelatin nanocomposite with gelatin OTR reduction by 21 and 36 % at 5 and 10 wt. % concentration of nanocellulose was reported by Mondragon et al. [188]. Similar results were observed utilizing CNC and CNFs individually. Though, high polymer film's crystallinity results in improved gas barrier behaviours. CNC have the utmost degree of crystallinity, and this result in enhanced barriers to gas molecules when compared to CNFs or bacterial nanocellulose (BNCs).

CNC as low as 2 % concentration in poly(3-hydroxybutyrate) (PHB) lessened the oxygen permeability of PHB films by 65 % [189]. The barrier property enhancement was determined by the amount of CNC in the film. Apparently, in order to hinder circulation of gases throughout the composite, it is advantageous to integrate the CNC into the bulk polymer matrix [190-191]. CNC has demonstrated its significance in oxygen barrier through incorporation in kappa carrageenan [192], collagen [193], poly(propylene carbonate) (PPC) and polyethylene glycol (PEG) [194], poly(L-lactic acid) and (PLLA) [195]. CNC has likewise demonstrated considerable resistance to oxygen when coated on PET [176]. The coatings/films produced from CNFs are slightly brittle than those fabricated from CNCs

notwithstanding the fact that minimal OTR results from elevated CNCs crystallinity. Obviously, the tortuous behaviour of NC which leads to reduction in gas molecules permeation employing composite films, is worthy of research for future prospects.

The available positions amongst the molecules alongside cohesive energy density of the equivalent, likewise informs the permeation ability of gas in a material. Incorporation of CNCs to a polymer matrix leads to higher cohesion energy as a result of a network of hydrogen bonds present. As well, the free volume and the chain mobility were lessened ascribed to the existence of nanoparticles [196-197]. The oxygen penetrability of virgin PLLA was reported to decrease by 66.4% upon 1 g of PEG and (0.5 wt. %) CNC addition [198]. 2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO)-oxidized cellulose nanocrystals was reported to function as oxygen blockades [199]. Composite systems with CNC and CNF were reported to decrease the OTR by a factor of about 260 and 300 in air resistance comparative to papers without coating [200]. Similarly, observed increased grease and oil resistance were comparable to the fluorochemicals. Due to credible hydrophobic and lipophobic behaviours of fluorochemicals, they are considered excellent food packaging material for non-stick and waterproofs [201].

#### 4.2. Water vapour barrier properties

The water vapour (WV) permeability of films is very essential and constitutes a major issue which instantly influences the circulation of oxygen across the film. Cozzolino et al. [202] reported a 20 times OTR increment at a relative humidity degree of about 80%, confirming plasticization of the film in the presence of water. Deterioration of film adherence at greater dampness by water molecules, results in increased rate of gas dispersion [203]. Some determinants influence water vapour transmission rate (WVTR) of a packaged polymer/composite film, which are crystallinity, pressure, temperature, thickness and film density, hydrophilicity, structure and pore sizes. However, in order to allow increment of food product's shelf life by the fabricated film, interaction with moisture needs to be avoided throughout the film transportation, application and handling. Research is comprehensively ongoing implementing NC as filler either in coatings, nanocomposite films or as a polymer matrix alone exclusively.

#### 4.2.1. Cellulose nanofibrils reinforced films

Barrier behaviours of nanocellulosic films stand to be extremely substandard for water vapour though, excellent for gases upon utilization when in unmodified state. For the purpose of packaging, polymer films are presumed to reduce vapour transference amidst packed product and the surrounding atmosphere. The water vapour permeability (WVP) is an essential factor which helps to forestall contamination of the packaged goods or contamination of the environment through the packed goods. The WVTR of CNF film was reported to be  $\sim 174 \text{ g/m}^2/\text{day}$  [204], a high value comparable to LDPE ( $\sim 15\text{--}20 \text{ g/m}^2/\text{day}$ ) [187]. Continuous researches on the improvement of water vapour barrier behaviours are ongoing, for instance, Sharma et al. [205] reported 50% reduction in WV when CNF film was heated at  $175^\circ\text{C}$  for 3h. The study also reported increased hydrophobicity and crystallinity of the CNF with reduced absorbency which hindered spreading of water molecules. Functionalized CNF with greater specific area and aspect ratio may result in system entanglement [206]. Though modification of CNF by TEMPO oxidation proves inadequate in water barrier properties with

$\sim 235 \text{ g/m}^2/\text{day}$  for 50% RH, notwithstanding the fact that it competes favorably with synthetic polymers in terms of resistance to gases (Fig. 12). Tempo oxidized CNF, PVA and Polypyrrole (PPy) nanocomposite films by in-situ polymerization and distribution of pyrrole over tempo oxidized CN/PVA films followed by polymerize was respectively reported [207–208]. In the first instance, EDX investigations revealed that PPy situated on the surface of the composite resulted in improved contact angle ranging from  $54.5$  to  $83^\circ$ , conforming to improved heat shield. In the later instance, the overall behavior of the film was evaluated over water vapor and gas barrier behaviours. The exterior layer containing PPy with its hydrophobic attribute, shields the film from penetration of water ( $18 \text{ g/m}^2/\text{day}$ ). The recorded better results compete favorably with the commercially available petroleum-based polymers of about  $16.8 \text{ g/m}^2/\text{day}$ . However, the reported film was assessed for food containing bacteria (*B. Subtilis* and *E. Coli*), and results revealed that the film performed as an active packaging on meat by killing the microorganisms at the interface upon slight leaching of PPy.

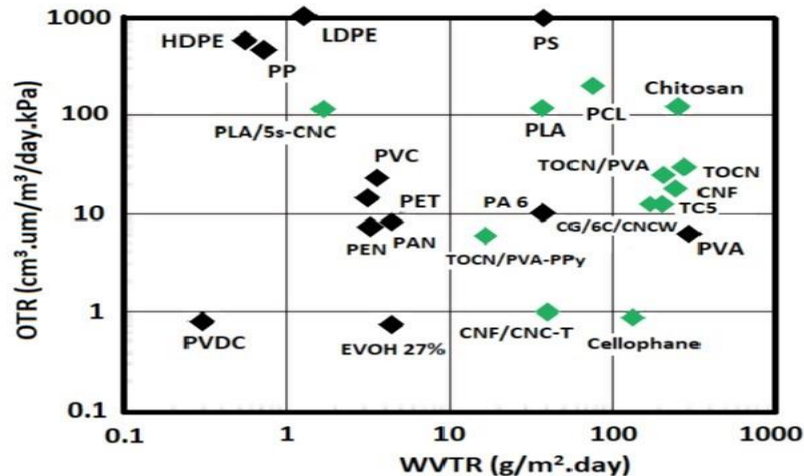


Fig. 12: WVTR and OTR of synthetic and bio-polymer nanocomposite films for packaging [209, 185] (Black bullets represents petroleum-based polymers while green bullets represent biopolymers)

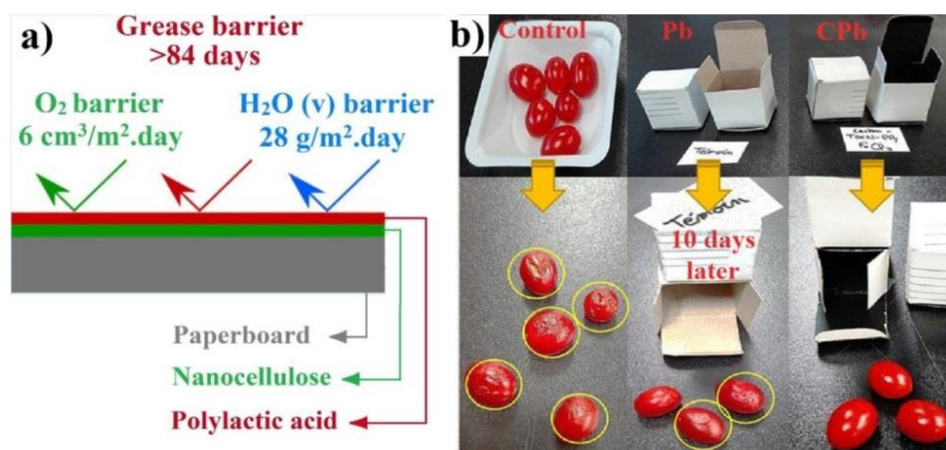
In recent times, studies are being focused on development of nanocellulose coating on sustainable biopolymers, thus producing packaging films that are absolutely biodegradable [10]. Presumably, an aqueous coating may function in the form of pure thin layer or composite in addition to frequently used materials with dispersible NC. NC has been utilized as a consumable coating material for

fruits, for example, CNC aqueous slurries coating on blueberries with calcium carbonate nanoparticles [210] or coated strawberries with a blend of 1 & 5% chitosan and NC [211]. The above coatings demonstrated improved performance in decreasing the seepage of anthocyanins, loss of weight and decomposition rates. Packaging applications of paperboards, targets elongation of the packaged food shelf life

and at the same time, lessening the package wastes [212]. On the other hand, sole utilization of paperboards for packaging of food is not worthwhile, as a result of vulnerable mechanical properties together with susceptibility to dampness [213].

Water vapour permeation rate can most likely be minimized by creating a multi-layered network, which could shield the inner material from moisture effects [214] above an underlayer. An example of multi-layered packaging was reported by Koppolu et al. [215], who formulated and further fabricated a thin multilayered NC coating reinforced with PLA as against a paperboard through slot-die and extrusion coating. In their report, NC reduced WVTR by 23%, notwithstanding 90% humidity and 38°C temperature. Moreso, NC reduced OTR and rate of heptane's transference by 98 and 99% respectively, in comparison to PLA-coated

and sole paperboards accordingly. Bideau et al. [216] reported investigations on the use of PPy and tempo oxidized nanocellulose (TONC) coating for food packaging. The coating was evaluated in comparison with paperboard without coating through storing cherry tomatoes for 10 days as shown in Fig 13(b). The tomatoes reserved within the coated paperboard maintained their textures and remained stable. Besides, the solid network structure created by combining TOCN and PPy, which provided a barricade over moisture and oxygen, was accountable for the observed packaging stability. However, the authors proposed recycling of about 80% of the paperboard by removing the layer of PPy. Fig. 13(a) represents a multilayered packaging system with restrictions on grease, oxygen and water.



**Fig. 13: Graphical illustration of (a) Multi Layered packaging system restraining grease, oxygen and water (b) Simulation of packaged cherry tomatoes in coated and uncoated paperboard for 10 days [215-216]**

## 2.2. Cellulose nanocrystals reinforced films

CNC remains an excellent coating material for packaging application, comparable to CNF. A study on the reinforcing capacity of CNC isolated from coconut fiber on coatings based on alginate-acerola puree was reported [217]. The study revealed that CNC reinforced film reduced the WVP, fruit weight loss, ascorbic acid loss and deterioration frequency by 30, 53, 70 and 46% successively. Significant improvement of coatings reinforced with CNC compared favourably with coatings reinforced with montmorillonite nanoclay, though, the latter provided enhanced fruit load holding ability. In recent researches, CNCs are employed extensively as fillers in biopolymer matrices for the fabrication of composite films for packaging

applications [47, 218]. Notwithstanding the fact that CNC and great number of biopolymers are hydrophilic in nature, literature has demonstrated improved water vapour barrier properties (WVBP) of nanocomposite with CNC incorporation [Dhar et al., 2015; George & Siddaramaiah, 2012][189; 219]. Oyeoka et al. [47] reported decreased WVP of polymer films ascribed to impermeable CNC, in a study on packaging and degradability properties of polyvinyl alcohol/gelatin nanocomposite films filled with water hyacinth CNC. Hydrogen bond formation between CNC together with several other biopolymers improves the compatibility of composite films and at the same time, hinders the formation of -OH groups that lead to water permeation. In addition, the thermo-mechanical



behaviour of nanocomposite films was enhanced by high crystallinity of CNC [220]. In order to enhance WVBP and oxygen barrier performance (OBP), uniform distribution of nanocellulose in polymer matrices needs to be guaranteed. However, one of the probable approaches for uniform dispersion is the use of surfactants that functions as a compatibilizer amongst the nanocellulose and hydrophobic polymer matrix and at the same time, hinders agglomeration of CNC [221]. Improved agglomeration and interaction of CNC with PLA boosted the polymer film's barrier properties. With 1% surfactant concentration within the nanocomposite film, oxygen permeation (OP) and WVP decreased by 26 and 34% respectively.

Polymer reinforced nanocellulose was reported to have decreased WVP and at the same time, enhanced moisture barrier behaviours [222]. Literature confirmed that cassava starch reinforced with nanocellulose exhibited lower WVP with greater tensile strength [223]. NC integration in biodegradable polymeric matrices and polysaccharides leads to reduction of WVP [174]. Chi and Catchmark [224] developed a ternary polysaccharide polyelectrolyte complex (PPC) material through high-shear homogenization, from CMC, chitosan (CS) and CNC, where CNC was cross-linked ionically to CMC/CS matrix. At 10 wt % CNC incorporation, the tensile strength and young's modulus were reported to be 60.6 MPa and 4.7GPa respectively, a 48 and 60% increment compared to virgin PPC film. A WVTR of 7982 g  $\mu\text{m m}^{-2} \text{d}^{-1}$  was recorded upon CNC addition, a 40% reduction compared to composite film without CNC. The PPC system imparted strong barrier against water, oil and grease diffusion on the paperboard substrate for one week, at <5 wt % concentration of CNC. The WVTR reduction was reported to be attributed to formation of thick packed structure by the CS/CMC matrix which hindered water vapour diffusion. The high crystallinity possessed by the CNC, strengthened the interlinkage alongside the matrix [217]. Analysis on the packaging behaviours of NC from different sources such as water hyacinth, bamboo, sisal and cotton linters were reported [47,225]. Starch polymer matrix was revealed to have significant effect with regard to environmentally friendly [226], though, the bamboo isolated NC/starch film gave minimum value of 27.6 and 32.9% with regard to water

vapour and oxygen permeability respectively, in comparison with virgin starch film. The observed decrease was reported to be ascribed to high crystallinity of bamboo isolated NC over sisal and cotton isolated NC [227].

#### 4.3 UV-barrier and antioxidant properties

Research interests on the development of irreversible and non-toxic O<sub>2</sub> sensors that can guarantee elimination of O<sub>2</sub> in nitrogen and vacuum food packaging systems have been on the increase. Substantial photochemical reactions resulting in free radical formation are triggered by UV radiations ranging from 315-400 nm (UV-A) and 280-315 nm (UV-B) [218]. The free radicals in turn initiate oxidation of proteins, vitamins and lipids, together with the degradation of antioxidants, colour/texture changes and off-flavors development. Consequently, vulnerability towards UV radiation brings about dropping of nutrition and organoleptic value, reduction in shelf life and foodstuffs value [228-230]. This emphasizes the significance of fundamental pursuit and antioxidant performance in food packaging applications [231]. Bideau et al. [208] reported lesser oxygen permeability (16.5 cm<sup>3</sup>/m<sup>2</sup>/day) with NC incorporation on a study of NC/PPy nanocomposites. Their reports also have it that the film was able to preserve bananas for five days with no sign of oxidation, probably as a result of antioxidant properties possessed by PPy. In a work reported by Bao et al. [232], nanocomposite film of Chitosan-xylan-CNC demonstrated improved antioxidant, antibacterial and mechanical properties where xylan served as an antioxidative agent. In the same way, Wang et al. [174] reported similar results with the utilization of epigallocatechin-3-gallate antioxidants in chitosan/BC nanocomposites. Luo et al. [233] produced aramid nanofibers (ANF)/CNF reinforced nanocomposite derived from paper-making methods. Reports showed that pure CNF demonstrated improved optical transmittance within the range of 400-800 nm, however, the UV protection remained substandard while absorbance seemed very small (200-400 nm). Aramid nanofibers have the ability to absorb UV emissions owing to the conjugated effect of benzenes and amide bonds together with display of elevated transmission in the visible spectrum. CNF film with 2% ANF was reported to exhibit outstanding UV protection with increased transparency. The massive quantity

of active groups present on ANFs surface makes cellulose matrix interfacial bonding feasible. On the other hand, strong CNF films could be fabricated through spray coating [234] or vacuum filtration [235].

Antioxidants are better incorporated to the packaging film instead of direct combination with the food. Packaging films comprising of polyphenols like murta leaf extracts, thyme extracts, grape seed extract etc. have been utilized for oxidation resistance in food packaging [236-237]. Wu, Deng, Luo, & Deng [238] reported a study on multifunctional film comprising tempo oxidized nanocellulose deactivated AgNPs with grape seed extracts (GSE). Result revealed improved UV protection, reduced transparency, antioxidant behaviour resulting from GSE and improved shelf life resulting from sluggish release rate (5.7% in 14 days) of antibacterial AgNPs. A study on hybrid nanobio-composite film with anionic tannin extracts and cationic CNFs (CCNFs) was reported [239]. Improved UV radiations absorbance was noted upon further addition of tannin mixtures ascribed to increased polyphenolics contained in the film. Nanocomposites with 90:10 (w/w) of CCNF and tannin engrossed about 100% of the UV radiations (wavelength < 320 nm) while, 95:5 (w/w) of CCNF absorbed about 92% of the radiations in the similar array. Extracts from tannin facilitated fuzziness reduction in the film. Assessment of antioxidant behavior of the film by 2, 2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging test, resulted in DPPH radical colour change, which faded slowly upon reaction with antioxidants and decreased the UV-light absorbance at 517 nm. Cazón et al. [240] prepared nanocomposite with PVA, glycerol and BC. The UV light (200-280 nm) transmittance of pure BC films was reported to be very low (1%) and approximately 7.5% at 400 nm. Upon glycerol addition, the UV light transmittance of the BC films decreased more to 0.57% at 200-280 nm, and later increased to utmost value of 7.5% at 400 nm. Results further revealed superior performance of the film in regard to transmittance compared to regenerated cellulose-glycerol-PVA films and regenerated cellulose- based films [241-243]. Addition of glycerol improved the plasticizing ability (with 98.8% reduction in young's modulus at 5 wt. % glycerol) of the composite whereas PVA recorded enhanced mechanical properties (with 17% Young's modulus

increment at 5 wt.% PVA) as reported. Consumable packaging film for potential oil bags using carboxylated CNC whiskers (C-CNCW) as reinforcement was reported by Cao et al. [185]. The UV-vis analysis of the film showed UV light within 200-280 nm. The closing capacity of the film was excellent (1295.40 N/m) for pure Cassian Gum (CG) film and 2218.78 N/m for CG with 4% C-CNCW. The values were reported to be greater compared to gelatin-based films with closing capacity of 500-870 N/m [244]. As well, reports have it that incorporation of C-CNCW to the CG films barely influenced its optical transparency. However, as a result of low aspect ratio, CNC recorded little impact on the transparency and this is beneficial in food packaging applications.

Development of UV-activated calorimetric O<sub>2</sub> signal that utilizes TiO<sub>2</sub> nanoparticles for methylene blue (MB) reduction photosensitization incorporating triethanolamine in a polymer encapsulation medium through UVA light was reported by Lee et al. [245]. The sensor was reported to be bleached and remained colourless upon UV irradiation until exposure to oxygen, after which its initial colour was restituted. The degree of oxygen exposure determines the rate at which colour is recovered. An easy chemical method applied to deposit oxides to several substrates involving MB/TiO<sub>2</sub> nanocomposite thin films on glass through liquid phase deposition (LPD) was reported [246]. This approach may possibly be employed in the development of an O<sub>2</sub> indicator packaging system for a range of oxygen-sensitive foods. A photo sensitizer (such as nanocrystalline SnO<sub>2</sub>) within a colorimetric O<sub>2</sub> indicator consisting of encapsulating polymer like hydroxyethyl cellulose, a redox dye (MB) and a sacrificial electron donor (glycerol) was utilized by Mills & Hazafy [247]. Results revealed activation (photobleaching) of the indicator and photoreduction of MB by SnO<sub>2</sub> nanoparticles due to exposure to ultraviolet B-rays light. The colour variation in films was dependent on O<sub>2</sub> exposure, bleaching occurred when not exposed while blue occurred upon exposure to O<sub>2</sub>.

### 5.0 Smart packaging

A system which identifies characteristic properties of packaged food and employs a mechanistic approach to record and disseminate findings regarding the present value and protective state of the food is referred to as smart food packaging system. On this

basis, nanostructures could function as responsive material particles for packaging applications. Nanosensors however, might react to environmental factors such as relative humidity, temperature or exposure to oxygen during the course of storage in addition to microbial infection and/or deterioration of products [248]. Expiration dates for packaged food are predicted through consideration of circulation, storing and environmental factors involved in the exposure of the food products. Though, these factors are not usually the actual ones. For example, foods that need a cold chain are frequently subjected to temperature exploitation, in which case, sealing defects or micropores in packaging networks could unexpectedly expose food products to high oxygen. Integration of nanosensors in food packaging systems might spot changes in relation to spoilage, biochemical contaminants and pathogen, which are helpful in eliminating any need of inaccuracies in expiration dates, and thus, supplying actual-time state of food freshness [249].

### 5.1. Discovery of food spoilage gases

Gases produced by microorganism's metabolism result in food decay and this might be observed through various kinds of gas sensors designed to interpret biochemical correlations among surface particles into response signals.

Detection of gases by nanosensors are normally based on metal oxides employed, and currently, on conducting polymer nanocomposites that have the capacity to enumerate and/or distinguish microbes with regard to their emitted gases. Conducting polymer-based sensors consist of conducting particles entrenched into a protective polymer matrix. The sensors yield a plan conforming to the gas under examination due to resistance changes [250]. Conducting polymers remain highly significant due to their optical, electronic, electrical and magnetic properties, associated with their conjugated  $\pi$  electron backbones [251-253]. Polyaromatic and polyene conducting polymers (polyacetylene, polyaniline and polypyrrole) were broadly investigated [252]. Conducting polymers produced through electrochemical polymerization possess outstanding capability to adjust between conducting oxidized (doped) and insulating reduced (undoped) conditions, and this is the foundation for numerous usages [254]. Fabricated carbon black and polyaniline

containing nanosensors was reported to discover and isolate three foodborne pathogens through establishing an explicit reaction model for individual microorganisms [250].

### 5.2. Sustainable Packaging

Sustainable packaging implies fabrication of packaging films employing viable materials, life cycle evaluations and records to moderate the environmental footprint and effects on packaged products. The sustainable packaging coalition

[<http://www.sustainablepackaging.org>] defined sustainable packaging as one that is:

- i. Advantageous, harmless and flourishing for individuals and societies all through its life cycle.
- ii. Measuring up to market standards for both efficiency and cost effectiveness.
- iii. Obtained, fabricated, conveyed and modernized employing sustainable energy.
- iv. Enhancing the utilization of sustainable basis materials.
- v. Fabricated by means of efficient manufacturing technologies and excellent approaches.
- vi. Manufactured from eco-friendly materials in every possible end of life circumstances.
- vii. Designed to substantially optimize resources and energy.
- viii. Effective recovery and usage in the organic manufacturing closed-loop cycles.

A study by Valdes et al. [255] reported that packaged waste amounts to 29.5% of the overall municipal solid waste (MSW) in 2009 in the USA and 25% of the entire MSW in Europe in 2006. Different regulations are being constituted by the government internationally to restrict the utilization of plastics in order to cut down the volume of packaging waste. For instance, the recovery and recycling of waste is encouraged by the packaging and packaging waste directives in Europe [256]. Packaging films developed from sustainable material is preferable as a result of growing awareness of environmental concerns. Integration of biobased packaging materials into the market is currently a new trend. Brand owners, retailers and packaging manufacturers are valuing and at the same time, growing more concern in high quality packaging materials for protection of their goods/products [257].

### **5.2.1. Principles of sustainable packaging**

The major objective of sustainable packaging is the incorporation of operational and advanced materials in packaging systems which boost financial and ecological health [258]. Packaging is planned and developed to satisfy controlling regulations, materials functionalization, analytical cost and market order. The project design begins with materials selection, a good knowledge of materials functionalization on product quality protection and imparting on the life span of the materials [259]. Material recovery for the minimization of generated packaging waste is the second principle of sustainable packaging. The major drawback associated with the growth of sustainable packaging is the effective recovery of packaging materials [260].

Biological recovery, technical recovery and energy recovery are some of the various methods obtainable for the possible assemblage and retrieval of packaging materials [260-261]. Continuous cycling of materials used for packaging with minimal material degradation is the third principle of sustainable packaging. Materials considered for packaging purposes ought to be strong to be continually reused [262]. The fourth principle is that the packaging materials should be clean and safe so as not to constitute danger to human life and ecosystem. Eliminating or minimizing the hazard associated with the packaging materials in addition to the life span evaluation of the packaging materials is the basic requirement of sustainable packaging [263].

### **5.2.2. Impact of nanocellulose materials in sustainable packaging**

Due to its high abundance, low weight and biodegradability, nanocellulose materials have been considered a remarkable engineering material [264-265]. Nanocellulose reinforced biocomposites possess improved mechanical and barrier properties. Being originated from natural resources, NC are virtually limitless, sustainable and widely substantial [265]. Nanocellulose does not use petrochemical components for its functionality nor interfere with the human food chain. Therefore, they have been used for sustainable and green packaging.

Fabrication of various polymer biocomposites reinforced with nanocellulose was reported [266-267]. Such properties as heat stability, biodegradability, specific surface area, transparency and gas barrier properties were enhanced. For sustainable packaging principles and strategies, nanocellulose is considered effective, and this effectiveness comprises minimum waste generation, maximum functionality and cost implication [18, 268]. Nanocellulose must be efficient, biodegradable, unsoiled and harmless, that is, able to minimize airborne and waste borne emission to the environment, greenhouse gas emission, toxicity and trash effect, to be considered for sustainable packaging [264].

### **5.3. Active packaging**

Packaging in which subsidiary substances have been deliberately included in or on either the packaging material or the packaging headspace to enhance the performance of the package system is called active packaging [269]. As a result of advancements in material science and nanotechnology, active packaging systems have gained popularity. Any active packaging system which releases antimicrobials or antifungal compounds into food chains during storage in order to aid rise in shelf life and fight foodborne illness is considered one of the largest sectors of technological development [270-271]. An example of an active packaging system is the oxygen scavengers.

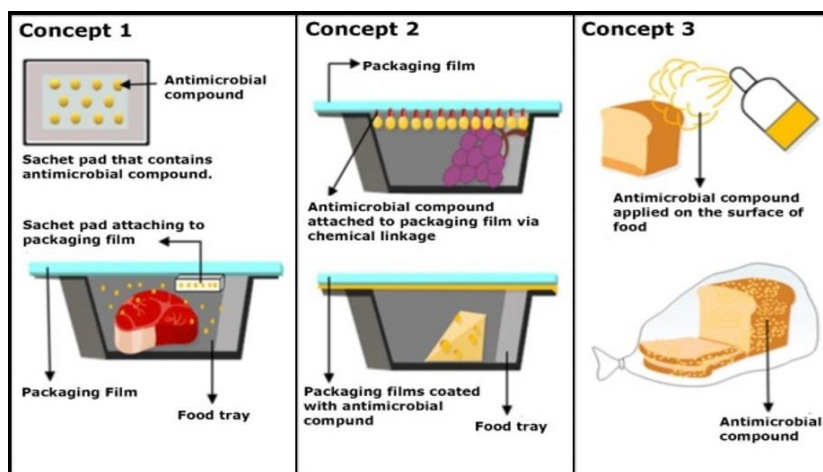
#### **5.3.1. Food packaging antimicrobial agent**

Eruption of foodborne ailments has inspired the world's consciousness on the need to prevent microorganisms from contaminating raw materials and refined foods. However, infested foods turn to waste and the ingestion of these infested foods could endanger the wellbeing of the end-users. Hence, impeding the actions of pathogenic microbes in food via active packaging was investigated and reported to conquer the said problems with the provision to offer healthier food products [272-273]. Active food packaging could perform several types of purposes such as flavouring, ultraviolet barrier, moisture absorber, oxygen scavenger, antioxidant and antimicrobial. Nevertheless, the release of functional biocide materials to food through active packaging has gained significant consideration as a result of the capability to elongate packaged food's service life in addition to reduction of the existence of foodborne



microbes. The antimicrobial activity may be achieved through addition of functional biocides squarely into food products or within the gap encompassing the packaged food. The primary purpose of antimicrobial packaging is to minimize and consequently, inhibit the proliferation of food decaying microorganisms [274]. There are various strategies of initiating active antimicrobial compounds into food packaging which were split into three ideas according to Appendini & Hotchkiss [275], Kapetanidou & Skandamis [276]. (i) Incorporation of the antimicrobial compound in

individual vehicles with no interaction between antimicrobial compounds and the packaged food (commonly experienced in meat packaging); (ii) Getting some segment of the antimicrobial complex restrained in the vehicles through indirect contact among antimicrobial compounds and food (e.g., envelopment of antimicrobial complex into biopolymer matrices); and (iii) introducing addition of antimicrobial complexes onto the food surface/core by direct interaction of antimicrobial complex with the food. The concepts for food packaging strategies are elucidated in Fig. 14.



**Fig.14: Antimicrobials in food packaging applications with (concept 1) interaction between antimicrobial compounds and the packaged food (Concept 2) indirect interaction among antimicrobial compounds and food and (Concept 3) direct interaction of antimicrobial complex with the food [277]**

Predominantly, antimicrobial compounds consist of two groups which may be organic or inorganic materials. The organic materials consist of natural polymers, enzymes or acids whereas the inorganic materials are metal oxides or nanoparticles. The variation with the above-mentioned antimicrobial materials is their thermal stability. The thermal stability of the former is lesser than that of the latter; hence nanoparticles of both metals and their oxides are likely to withstand harder fabrication situations [278]. Integration of nanoparticles containing antimicrobial agents seemed to consequently contribute immensely in food conservation advancements. Presently, utilization of nanotechnology, especially in the food section, seemed monopolized by packaging materials [47]. Application of nanotechnology in food packaging may be grouped into two various types, which are active and improved packaging. Active packaging comprises direct interrelation among nanoparticles and food products and/or environment, for attainment of higher safety level in food products, while improved packaging may

be attained when nanomaterials are integrated into polymer matrices in order to improve barrier behaviours. In the meantime, metal nanoparticles are more beneficial with regard to thermal stability. They could therefore be investigated for utilization as anti-microbial complexes for active packaging. Some metal nanoparticle antimicrobial carriers have been reported comprising Cu, Au, Zn, Ag and Ti. However, silver nanoparticles (AgNPs) showed greater antimicrobial behaviour in comparison with other metal nanoparticles [278]. The nano-sized AgNPs gives a greater surface area which facilitated interrelation between the nanoparticles and the microbial cells, hence, attained a prospective proficient antimicrobial behaviour in comparison with ordinary Ag particles [279-280]. Additionally, nanosilver holds broad-spectrum antimicrobial characteristics, and therefore, remains functional compared to antibiotic or multidrug resistance microbes [280-282].

The operation of antimicrobial behaviour of AgNPs is yet to be evidently identified, despite

numerous researches being carried out on its antimicrobial performance; hence, it continues to be a topic for investigation. Primarily, a couple of approaches are proposed for AgNPs: (i) Accumulation and binding of the silver nanoparticles to the cell wall together with the membrane proteins, which forms pits on the cell and ultimately infiltrates the cell, subsequent to destruction of the microbial cell structure that brings about demise of cells [283-285], (ii) Disconcerting the stableness of biomolecules and intracellular networks like DNA, through penetration of silver nanoparticles. The interrelation of silver nanoparticles with microbial cells could be described as the reactivity of weak acid with a weak base since the cells consist mostly of sulfur and phosphorus that function as a weak base while silver may serve as a weak acid. As well, the DNA backbone consists of phosphorus particles, permitting the silver nanoparticles to freely react with the weak base and ultimately damage the DNA. This situation activates a protective approach where the bacteria shields its DNA from destruction and ultimately limits self-replication of the cells [271,286,285], (iii) Disruption of essential cells by  $\text{Ag}^+$  through aiming and bonding to the thiol groups (ASH), which grasps the disulfide or sulfhydryl active groups on the enzymes or exterior of the membrane proteins. Connecting  $\text{Ag}^+$  ions to thiol groups establishes firm SAAg linkages that result in disablement of the protein. This activity hinders their entire performance in the microorganism [271,287](iv) Development of exorbitant AgNPs and  $\text{Ag}^+$  based reactive oxygen species (ROS) from

which will create disparity of oxidation/antioxidation, resulting in oxidative stress, swelling and consequent damage in proteins, membranes and DNA [280] and (v) Inhibition of the signal transduction and cell development, through damaging of phosphotyrosine history of bacterial peptides by the silver nanoparticle [283,284]. Fig. 15 elucidates the likely nanosilver antimicrobial approach. The present applications of nanotechnology in the food segment have been overtaken by food packaging materials which originated from nanotechnology.

Besides, as nanomaterials continue to gain commercialization and awareness on the environmental impact of plastic remain on the increase, biodegradable food packaging materials will advance to standard [288-289]. Food packaging derived from nanotechnology could be gotten by blending bio-based nanocellulose with antimicrobial reactive agents which originates from either natural resources or metal nanoarchitectures. Coalition of these two nanomaterials advances to eco-friendly bio-nanocomposites with improved anti-microbial behaviour. Furthermore, utilization of biopolymer matrices like polylactic acid (PLA) for eco-friendly nanocomposite, combined with antimicrobial and cellulose nanocrystals, the resultant nanocomposite could develop into excellent packaging material which can safeguard the food against microorganisms, and at the same time, tackle the problems of buildup of agricultural waste and environmental pollution.

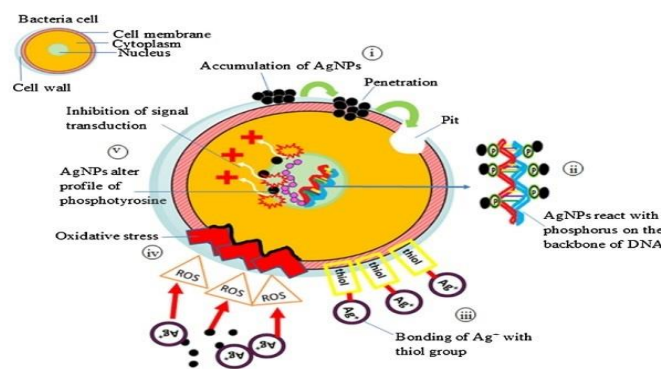


Fig. 15: Potential antimicrobial process of nanosilver [277]

#### 5.4. Intelligent packaging systems

This system monitors certain aspects of the food product and reports information to the consumer. Improving quality or value of product, providing convenience and tamper or

theft resistance is the purpose of the intelligent system. This however, depends on incorporation of sensors or sensor's network on the packaging material for actual period and constant performance evaluation.

#### 5.4.1. Thermoresponsive and mechanoresponsive intelligent systems

Time-Temperature Indicator (TTI) is the most leading thermoresponsive packaging design in use. The TTI can tell the consumer when foods have been temperature abused. It however, displays temperature variation alongside the duration of product exposure to the purposed temperature [290]. The time temperature indicator sensors could be derived from enzymes, functionalized materials or nanoparticle reactions which are developed to demonstrate whether the food products were subjected to temperature conditions favourable for microbial or fungal development [291-292].

Mechano responsive intelligent system (MIS) is another packaging system of interest. This system senses how food is mishandled or compromised during transportation. MIS functions as applied mechanical force which is utilized to trigger chemical reactions concentrate or dissimulate tiny particles or automatically break down chemical bonds [293]. Mechanoresponsive crystals were designed to alter the colour of their incandescence upon application of shearing or elongation forces [294]. Mechanoresponsive systems are yet to find practical application in food packaging. However, Hill et al. [295] explored the use of polydiacetylene (PDAs) based impact sensors for food packaging. In his study, an outstanding chromic change from deep blue to bright red, followed by a distinctive alteration in the Raman spectra of the PDAs was observed, which was reported to have resulted from environmental forces, like mechanical shear, heating, exposure to solvents etc.

#### 5.4.2. Chemoresponsive intelligent packaging systems

These are intelligent schemes activated through non-food chemicals. The said chemicals comprise toxins with non-biological by-products of bacteriological or fungal actions such as acids or gases. These non-food chemicals can be in the form of contaminants, biogenic chemicals or gases [296].

The contaminants can be chemical toxins introduced during production, processing, transportation or storage. One good instance is the food packaging disinfectant hydrogen peroxides. Biogenic ions such as  $\text{Cu}^{2+}$ ,  $\text{K}^+$  and

$\text{SO}_4^{2-}$  have been detected by tuning hydrogel with fluorophores [297]. Detection of biogenic gases is the most popular use of chemoresponsive packaging systems. Oxygen, carbon dioxide and ethylene are considered excellent indicators of decomposition having been formed or devoured by bacteria. Cavallo et al. [298] developed a calorimetric polypropylene sensor for discovery of reducing elements formed by milk decomposing bacteria. Removal of oxygen by bacteria results in colour change (colourless) by dye bromophenol blue sensor. Measurement of the amount of volatile organic compounds (VOCs) released by decomposing bacteria was achieved with the development of in-package sensor for fish decomposition [299-301].

Considerable attention has been given to the discovery of carbon dioxide in modified atmosphere and conservative packaging [302-303]. Dessert packages were incorporated with pH responsive materials to quantify decomposition through headspace  $\text{CO}_2$  investigation [304]. Measurement of headspace  $\text{CO}_2$  was achieved through a combination of pH indicator and phosphorescent reporter dye which enhanced its sensitivity [305]. A printable oxygen sensor which uses photocatalyzed oxidative dyes has been developed [306-307]. The blue dye becomes bleached when exposed to UV light and the colour recovery is related to oxygen content. Roberts & Holder [308] developed another indicator based on electrochromic polyviologen films. The film changes from pale to highly coloured surface in addition to an electronic pulse. However, the colour change was influenced by  $\text{O}_2$  reduction. The films are less susceptible to leaching into food products unlike the dye-based sensor.

#### 5.5. Responsive packaging (RP)

Responsive packaging may possibly be packaging consisting of an indicator that supplies information on the quality of food and microbiological activities [309]. This could be attained via employing various time temperature indicators, gas indicators, biosensors and barcode tags that can detect and report whatever interior or exterior alterations within the environments of the food products [310-311]. Responsive packaging is frequently referred to as intelligent packaging, smart packaging or bio-sensing. A study on the fabrication of bottom-up built (in-situ

polymerization) composite film comprising poly(sulfobetaine methacrylate) (PSBMA), a zwitterionic polymer exhibiting polyelectrolyte and anti-polyelectrolyte characteristics within the nanofibrous structure of BNC was reported [312-314]. The packaging film produced suggests applicability in monitoring the humidity levels of moisture irritated food products (such as dry foods, meat products or dairy products). Results reported variation in the composite's proton conductivity within the range of  $1.5 \times 10^{-4} \text{ mS cm}^{-1}$  (at 60% RH, 40 °C) to  $1.5 \text{ mS cm}^{-1}$  (at 98% RH, 94 °C). Protonic conductive based composite films possessing significant quality for intelligent packaging, which supports protonic-conduction humidity, sensing was reported [315]. Furthermore, improved water-uptake capability within the range of 450-559%, thermal stability (up to 265 °C) (in nitrogen environment), enhanced mechanical behaviours (young's modulus  $\geq 3.1 \text{ GPa}$ ) and barrier against UV radiations were likewise reported. The composite films were reported to successfully inhibit *E. coli* and *S. aureus* bacteria.

Sobhan et al. [316] incorporated the idea of bio-sensing into smart packaging application through fabrication of composites with active nanocellulose and activated carbon (NAC), to provide a combination of electrochemical potentials of activated carbon (AC) and thermo-mechanical potentials of functionalized nanocellulose. The condition of the food upon biochemical and bacteriological actions could be observed simultaneously with the aid of freshness indicators. Visible examination (indicator colour adjustment), which results from metabolites and indicators' reactions, instituted the foundation for the food's cleanness determination [317]. An intelligent pH examination tag was conceived by mixing bacteria nanocellulose with red cabbage anthocyanin extracts (32 and 193 mg L<sup>-1</sup>) [318]. The indicator, comprising dilute anthocyanins, was reactive to pH 2-10 with distinctive colour adjustment at various pH values. The colour reception effectiveness of the film remained directly affected by the moisture absorption of the film's pH indicator. Upon incorporation of dilute reddened cabbage anthocyanin extract, almost 15% increment in moisture absorption and 69% increase with concentrated anthocyanin extract addition was achieved. On the other hand, reports have it that the mechanical properties (Ultimate tensile

strength and Modulus) of the former were superior to the latter.

## 6. CONCLUSION

Nanocellulose from sustainable resources are biodegradable, widely obtainable and viable packaging material. Though, utilization of only NC in food packaging is not yearned for, since it exhibits poor resistance to water vapour and hence, not appropriate for a highly humid environment. The use of NC in polymer films and coatings improves the barrier properties such as gases and water vapor of nanocomposite packaging films. However, in order to achieve excellent packaging film from NC, chemical surface modification performed somewhat so that it does not alter the integral properties of the NC, is obligatory. The fabrication of eco-friendly food packaging materials in addition to the performance of different antimicrobial sources with NC, in packaging films has laid on the development of innovative ideas in antimicrobial packaging, contributing countless benefits in antimicrobial packaging (AP) systems. Identification of novel functional sources that are receptive contrary to a broad range of microbes is essential in AP schemes. Due to the fact that a significant quantity of antimicrobial agent in food is highly restricted with regard to principles, attention on emigration performance of said antimicrobial vehicles is needed. For instance, AgNPs has an upper limit of 0.05 mg/kg on food with regard to the European Food Safety Authority. Over the years, research is focused on manufacturing of functional biodegradable films utilizing entirely eco-friendly approaches which do not involve the use of chemically reducing agents such as plant extract reduction and UV reduction approaches. Bacteria nanocellulose with its high-performance in food packaging applications, is by no means, widely discovered due to exorbitant fabrication cost, which is a major obstacle, hence, commoditization of the packaging market remains a big task. Although substantial improvements were recorded while stability with regard to environmental impact, cost effectiveness, efficiency upon usage and the shelf life of the films have not yet been achieved, hence more attention is required. Despite the fact that recent approaches have confirmed the possibilities of employing NC for controlled release of antimicrobial agents, utilization of bio-polymeric raw materials with the required barrier properties and attaining the food



packaging necessities remains a major issue to surmount. To explore NC in marketable packaging, engineers and material scientists ought to be in partnership. The predominant engagement of sustainable and biodegradable nanocellulose to replace its plastic equivalent will certainly promote conservatory gas minimization.

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